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Materials Characterization Center

A State-of-the-Art Review of Materials Properties of Nuclear Waste Forms

April 1981

Prepared for the U.S. Department of Energy
under Contract DE-AC06-76RLO 1830

Pacific Northwest Laboratory
Operated for the U.S. Department of Energy
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MATERIALS CHARACTERIZATION CENTER

A STATE-OF-THE-ART REVIEW OF MATERIALS PROPERTIES OF NUCLEAR WASTE FORMS

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April 1981

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FOREWORD

The Materials Characterization Center (MCC) was established at the Pacific Northwest Laboratory to assemble a standardized nuclear waste materials data base for use in research, systems and facility design, safety analyses, and waste management decisions. This centralized data base will be provided through the means of a Nuclear Waste Materials Handbook. The first issue of the Handbook will be published in the fall of 1981 in looseleaf format so that it can be updated as additional information becomes available. To ensure utmost reliability, all materials data appearing in the Handbook will be obtained by standard procedures defined in the Handbook and approved by an independent Materials Review Board (MRB) comprised of materials experts from Department of Energy laboratories and from universities and industry.

In the interim before publication of the Handbook there is need for a report summarizing the existing materials data on nuclear waste forms. This review summarizes materials property data for the nuclear waste forms that are being developed for immobilization of high-level radioactive waste. The information was compiled for the MCC mainly by PNL staff. It is intended to be a good representation of the knowledge concerning the properties of HLW forms as of March 1981.

Some general comments about the content of the compilation follow:

Organization. The contents of this report are arranged according to materials property. Data for as many different waste forms as possible are included for each property, but in many cases the data are preponderantly for borosilicate glass because that waste form has been so much more thoroughly characterized than the others. For the sake of brevity, detailed waste form compositions are included with the corresponding data only when it is necessary for clarity. But users of data in this report are cautioned that most waste form properties are quite composition-dependent; thus source references from which the individual materials compositions can be obtained are included with all the data. At the risk of repetition, the authors have listed the references with each section.

Radioactive Waste Forms Included. Waste forms being developed for the immobilization of high-level waste are emphasized in this report; however, these waste forms may also find application for the immobilization of intermediate-level, transuranic (TRU) and low-level wastes. It is very important to emphasize that much of the materials property data compiled in this report has been obtained from laboratory-prepared material, often with nonradioactive isotopes substituted for the radioactive isotopes in actual nuclear waste. For many of the materials properties, confirmatory data obtained on waste forms fabricated under realistic conditions with representative levels of radioactivity are much to be desired.

Measurement Methods. Measurement methods used to obtain much of the materials property data are briefly described in this report. These descriptions are necessary because standard techniques have not yet been adapted for measuring many pertinent materials properties of nuclear waste forms. (The MCC is in the process of defining such standard measurement techniques.)

Relationship of Waste Form Materials Properties to Criteria. The overall criteria to which nuclear waste forms must be designed depend upon requirements specified by the Environmental Protection Agency (EPA) and the Nuclear Regulatory Commission (NRC). The requirements of both agencies, which are in the late draft stages, allow a great deal of flexibility in waste form design since they set specifications only on release to the biosphere (EPA's draft 40 CFR 191) or from the boundaries of a geologic repository (NRC's draft 10 CFR 60). The only requirements for the waste form itself are given in draft 10 CFR 60, and these are quite general in nature. The waste form shall be:

- solid
- consolidated (not easily dispersed)
- noncombustible
- nonexplosive
- nonpyrophoric
- contain no free-standing liquid.

Since there are no performance objectives for the waste form per se, developers of waste forms have tended to emphasize comparison of waste forms, either with properties of other waste forms or with the properties of materials known to exhibit desirable long-term stability.

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The authors gratefully acknowledge the helpful counsel of too many colleagues in the nuclear waste form development field to be mentioned individually. O. F. Hill and W. A. Ross contributed significantly to the initial stages of the document. The editorial and production assistance of J. A. Powell and S. C. Cozad is also gratefully acknowledged.

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1.0 INTRODUCTION

This report is a state-of-the-art review of the materials properties of the nuclear waste forms that are being developed for the immobilization of high-level radioactive waste. The U.S. DOE and its predecessor agencies have had a long-standing effort in this field, as have similar governmental agencies in most other major industrial nations of the world. Thus there are a multitude of waste forms that have received at least some development, and a large amount of materials data on these forms can be found in the literature. It is only in the last 5 to 8 years that the measurement of waste form property data has become relatively sophisticated, however; thus the information compiled in this summary is selected from that time period.

1.1 WASTE-FORM CATEGORIES

The data compiled in this report apply to four major waste form categories: glasses, high-fired crystalline materials, low-temperature crystalline materials, and composites. There are many variants within these major categories, and acronyms are often used in the literature for some of them. A brief discussion of the waste form categories and some of the acronyms that will be found in this compilation follows.

Glasses. The preponderance of data in the compilation is for borosilicate waste glass formulations that are processed at temperatures between about 950 and 1150°C, because more development of this waste form has been done worldwide than of any other. The glasses are designed to be cast as "monoliths" in cylindrical steel canisters approximately 3 m long and ranging from approximately 0.3 m in diameter for HLW from the commercial fuel cycle to approximately 0.6 m in diameter for the lower heat-producing HLW from military programs. The principal variants on the borosilicate glass formulations are to reduce the boric oxide content, substituting alumina or more silica in order to form glass-ceramic or high-melting formulations. Glass-ceramic waste forms are purposely devitrified, or crystalized, to increase thermodynamic stability and may contain 50 vol% crystals. High-melting waste glasses would require processing temperatures of 1350°C, or higher, if processed by standard glass-melting technology, but techniques for lower temperature processing using porous glass matrix or sol-gel technology are being developed.

High-Fired Crystalline Materials. This is a large category of waste forms that has as its common denominator a high-firing step, almost always above 800°C, and usually nearer 1200°C, that produces a water-free product of almost theoretical density. "SYNROC (synthetic rock)," "super calcine," "tailored ceramic" and "titanate" waste forms belong in this category. Hot-pressing, hot isostatic pressing (HIPing), and cold-pressing and sintering are among the high-firing techniques utilized in the manufacture of these waste forms.

Low-Temperature Crystalline Materials. These are principally concrete- and clay-based waste forms which, because they retain some chemically bound water, are probably more suitable for defense HLW than for the higher-heat-producing commercial HLW. FUETAP, meaning concrete formed under elevated temperature and pressure is an acronym for a waste form belonging in the category of low-temperature crystalline materials that will be encountered several times in this compilation report.

Composites. This is a large, multifarious waste-form category. It includes cermet, coated-particle and metal-matrix waste forms. Cermet and metal-matrix waste forms are somewhat similar; however, in cermets the dispersion of waste particles in the metal is on a micrometer scale, whereas in metal-matrix waste forms, large particles--generally between 0.1 and 1 cm in diameter--are dispersed in the metal, which is generally a lead or aluminum alloy. Particles of any waste form, including waste glass in the form of beads, can be dispersed in metal matrices. Coated-particle, or multibarrier, waste forms feature coatings of inert materials such as pyrolytic carbon, silicon carbide, or alumina on spherical particles of a core waste material. The coated particles are in turn dispersed in a metal matrix.

Recent references that describe the various waste forms in more detail include DOE/TIC-11219 (1980), Treat et al. (1980), and Shulz et al. (1980).

1.2 IMPORTANT WASTE-FORM MATERIALS PROPERTIES

Although there are no quantitative performance criteria for HLW forms, there is general agreement on the materials properties that are important, and on the fact that changes in these properties with time, as influenced by temperature and radiation, must be understood. For the purposes of this data compilation, the materials properties are divided into seven major groupings.

Physical Properties. These are bulk materials properties, such as density and thermal conductivity, that are needed for basic engineering design of the waste management system; they affect risk analyses only peripherally.

Mechanical Properties. Waste forms are not structural materials; thus their mechanical properties are not of principal importance. But waste forms are required to be consolidated and resistant to dispersion (i.e., powders, although solids, are not acceptable waste forms). The mechanical properties measured on waste forms are directed toward defining their coherence and impact resistance.

Chemical Durability. This is the most important waste form property; waste forms are designed to have the maximum practicable chemical durability. Chemical durability is usually thought of as leach rate of a given waste form in a water environment, but its complete definition requires an understanding of other factors such as solubility constraints.

Vaporization. Vaporization of radionuclides from waste forms is a potential dispersion pathway that must be considered in risk analyses. Dispersion by this pathway could occur in some accident situations involving high temperature. Analysis of these accident scenarios requires data on the identity and amount of radionuclides that can potentially vaporize.

Radiation Effects. Perhaps the most unique materials aspect of HLW forms is the high level of continuing self-irradiation they will receive. The effects of this irradiation for thousands of years into the future need to be understood. Accelerated techniques of producing radiation effects are used to estimate the long-term behavior of waste form materials.

Phase Stability. Concomitant with self-irradiation is self-heating, which can cause phase transformations in crystalline waste forms and devitrification of vitreous waste forms. It is important to know the extent of these effects and whether or not they result in any degradation of waste form materials properties.

Data for each of the preceding seven major groupings are presented in the remainder of this report. The data are not all-inclusive. Instead the emphasis is on providing a comprehensive summary of representative materials properties for all of the waste forms for which sufficient good-quality data exist.

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2.0 PHYSICAL PROPERTIES

M. D. Merz

The physical properties of waste forms depend on chemical composition, manufacturing technique, and storage conditions, in rapidly descending order of importance.

The overall chemical composition of high-level nuclear waste forms is determined by the composition of their two principal components, 1) the stabilizing inert constituents that are added to produce coherence and influence the overall microstructure and 2) the nuclear waste constituents. The proportion of nuclear waste constituents in the waste form is usually expressed as "waste loading," in units of weight percent. The waste loading of most waste forms is ~33 wt%, but it can vary widely, from a few percent to almost 100%. Waste loading is not an expression of radionuclide content: although immobilization of the radionuclides in nuclear waste is the raison d'etre for waste forms, nonradioactive isotopes greatly predominate in mass, especially in defense HLW but even in commercial HLW. Radionuclide content can be obtained only from detailed knowledge of the composition of the waste and its age, since the radionuclide content decreases with time. A good compilation of representative nuclear waste compositions was published recently by Mitchell (1980).

The physical properties compiled in this section were measured on laboratory-prepared specimens, but are thought to be fairly representative of materials that would be produced by the proposed full-scale manufacturing techniques for the various waste forms. An additional caveat is that the specimens did not contain actual wastes; instead they contained "simulated" wastes that use chemically similar nonradioactive standins for the radionuclides. This is not thought to detract from the relevance of the data. Earlier studies have shown a good correspondence between physical properties measured on waste forms with simulated wastes and with wastes containing the actual radionuclides (Mendel and McElroy 1972).

2.1 DENSITY OF WASTE FORMS

Table 2.1 summarizes the data concerning density of waste forms. The measurements were almost always made by some variation of the Archimedes/buoyancy method.

TABLE 2.1. Density of Waste Forms

Waste Form	Density, g/cm^3	Reference
Glasses		
Borosilicate 72-68 high zinc 26% waste	3.4	Mendel et al. 1977
Borosilicate 76-68 33% waste loading	3.0	Mendel et al. 1977
Borosilicate 76-183 33% waste loading	3.1	Mendel et al. 1977
Borosilicate 76-375 33% waste loading	3.1	Mendel et al. 1977
Celsian glass ceramic 20% waste loading	3.10	W. Lutze et al. 1979
Fresnoite glass ceramic	3.7	W. Lutze et al. 1979
Glass ceramic (clay calcine)	1.51	Healey et al. 1979
Borosilicate glasses	2.83 to 2.86	Guber et al. 1979
Borosilicate glasses	2.6 to 2.8	Lutze et al. 1979
High-Fired Crystalline Materials		
Hot-pressed or sintered PW-9 100% waste loading	3.55	Wald et al. 1980
Sintered PW-9/frit 50% waste loading	2.21	Wald et al. 1980
HIP PW-9 100% waste loading	2.90	Wald et al. 1980
Sintered SPC-5B 50% waste loading	1.62	Wald et al. 1980
Ceramic (pollucite from BP clay)	1.71	Healey et al. 1979
SYNROC ceramic 10% waste		Ramm and Ferenczy 1981
Cold-pressed 310 MPa hot-pressed 1250°C at 6.9 MPa	4.33	
Sintered 20 hr	4.12	
Sintered 500 hr	3.95	
Low-Temperature Crystalline Materials		
Cement + 10% PW-9 waste	1.71	Wald et al. 1980
Cement + 5% SPC-5B	1.85	Wald et al. 1980
FUETAP concrete 15 to 25% waste sludge	1.69 to 1.76	Blanco and Lotts 1980a
FUETAP concrete 0.9 to 0.7 water/cement 15% waste	1.75 to 1.98	Blanco and Lotts 1980a
FUETAP (wet) 15% waste	2.17 to 2.26	Blanco and Lotts 1980b

2.2 THERMAL CONDUCTIVITY

Ranges of thermal conductivity of waste forms are given in Table 2.2.

TABLE 2.2. Thermal Conductivity Ranges of Waste Forms

Waste Form	Thermal Conductivity, W/m K	Reference
Glasses		
Borosilicate glass 72-68	0.84 to 1.21 (25 to 400°C)	Mendel et al. 1977
Borosilicate glass	1.2 to 1.4	Lutze et al. 1979
Phosphate glass	0.8 to 1.2	Lutze et al. 1979
Glass-ceramic Celsian and fresnoite	1.2 to 1.4	Lutze et al. 1979
Low-Temperature Crystalline Materials		
High-alumina concrete (HAC)	0.33 to 1.21 at 100°C 0.51 to 0.63 at 200°C	Brookhaven National Laboratory 1974a; Colombo et al. 1975; Stone 1977; Brookhaven National Laboratory 1974b
IP concrete	0.71 to 0.86 at 100°C 0.62 to 0.92 at 200°C	
FUETAP	0.58 to 0.80	Blanco and Lotts 1979 Blanco and Lotts 1980

2.3 THERMAL EXPANSION

Thermal expansion coefficients for waste forms measured by conventional dilatometry are briefly summarized in Table 2.3.

TABLE 2.3. Summary of Thermal Expansion Data

Waste Form	Coefficient of Thermal Expansion, K-1	Reference
Glasses		
Borosilicate glass	8.0 to 12.0 x 10^{-6}	Guber et al. 1979 Lutze et al. 1979 Mendel et al. 1979
Glass ceramic Celsian and fresnoite	8 to 10 x 10^{-6}	Lutze et al. 1979
Low-Temperature Crystalline Materials		
Structural concrete (with aggregate)	9.9 x 10^{-6}	Zoldners 1971 Portland Cement Association 1979

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3.0 MECHANICAL PROPERTIES

M. D. Merz

Waste forms should remain as coherent and monolithic as possible during handling and transportation and when subjected to the forces resulting from subsidence and other processes in the repository. Thus, data on both impact and static strengths are relevant to selection and prediction of performance of candidate waste forms. Fracturing of the waste form under impact or static conditions increases the surface area that is potentially available for leaching in the event that water contacts the waste form. The amount of respirable fines (usually defined as particles with aerodynamic diameters <10 μm) produced during the impact fracture process is information used in risk assessments of potential accidents involving the waste form, particularly transportation accidents.

3.1 IMPACT RESISTANCE

Impact tests have been of two types, tests in which the waste form was constrained in a canister during impact and tests in which the bare waste form was impacted. The latter tests can be performed conveniently in the laboratory and are valuable for comparison purposes; the former involve more realistic boundary conditions and more closely approximate real accidents.

3.1.1 Tests of Canisters plus Waste Glass

Impact tests conducted by Smith and Ross (1975) on encapsulated waste glass tested both the canister (304 L stainless steel) and the borosilicate waste glass. In the tests, 10 cm long x 5 cm dia and 150 cm long x 15 cm dia canisters were impacted. The glass was a nonradioactive type 76-78 (simulated PW-4b-2) glass. Impact velocities were as high as 13.2 m/sec (44 fps) for the larger canisters and as high as 35 m/sec (117 fps) for the smaller canisters. Data were also obtained for test temperatures from 25 to 425°C.

Sieving analyses were used to determine particle size distributions. The weight fraction <10 μm was 10^{-4} for 36 m/sec impact velocity. The surface area increased by a factor of 40 for 36 m/sec impact velocity. Other data for various impact velocities and test temperature were reported.

3.1.2 Impact Tests of Small Waste Form Specimens

Impact tests of small, bare waste forms have been performed, with the fines produced being analyzed by sieving, Coulter counting, or sedimentation. In these tests right-circular cylinders of 1 to 3 cm length and 1 to 3 cm dia were impacted and crushed by a falling weight incident on the flat end of the cylinders. In some cases, multiple impacts were used to achieve desired total energy input; thus the tests also involved a grinding interaction subsequent to the initial fracture by impact.

Wallace and Kelley used a height of 0.8 m with weights to 2 kg. They did sieving analyses between multiple impacts on the same sample to obtain particle size distributions versus input energy. Analyses of particles <120 μm were done with a Coulter counter.

Bunnell used a height of 1.3 m with weights to 18 kg. He used multiple impacts but analyzed only once for particle size on each specimen, after the final impact. He concluded that multiple impacts were not equivalent to a single impact of the same total energy input (input energy = energy of falling weight = weight x height). He found that fines production per unit energy input was smallest for a single impact. Bunnell used sieving for particle analysis at sizes >44 μm and sedimentation analyses for smaller particles. Similar tests were done by Ramm and Ferenczy on SYNROC ceramic.

Mecham, Pelto and Jardine (Steindler 1980) have studied Pyrex® glass and have demonstrated the occurrence of log-normal size distributions for crushed cylinders. They used a weight of 0.88 kg at a height of 1.92 m. No data were reported on waste forms though their analysis of Bunnell's data on glass frit demonstrates the applicability of the log-normal size distribution to this particular waste form.

3.1.3 Impact Data

Impact data are summarized below in Table 3.1.

®Pyrex is a registered trademark of Corning Glass Works, Houghton Park, Corning, New York.

TABLE 3.1. Impact Data

Waste Type	Impact Energy/ Volume	Impact Velocity	Wt% Fines <10 µm	Surface Area Produced / Impact Energy	Surface Area Increase (ratio new/old)	Reference
Borosilicate (72-68)	Edge on impact at speed shown, canister + glass	7.6 m/sec 36 m/sec	0.001 2		1.3 to 3 10 to 100	Smith and Ross 1975, pp. 76, 81
ICM-11 PW-7-2 calcine	217 J/1.14 cm^3	4.88 m/sec	2.4	16 cm^2/J	574	Bunnell 1979
Borosilicate glass + sludge	78 J/3 cm^3	5 impacts 2 kg-0.8 m	0.0(a)	9.5 cm^2/J	58	Wallace and Kelley 1976
HAC concrete	94 J/5.86 cm^3	5 impacts 2 kg-0.8 m	1	7.3 cm^2/J	39	Wallace and Kelley 1976
HAC + 40% sludge	94 J/5.68 cm^3	5 impacts 2 kg-0.8 m	0.1	28.9 cm^2/J	154	Wallace and Kelley 1976
IP concrete	94 J/6.13 cm^3	5 impacts 2 kg-0.8 m	0.15	10.3 cm^2/J	55	Wallace and Kelley 1976
IP concrete + 40% sludge	94 J/5.65 cm^3	5 impacts 2 kg-0.8 m	0.4	19 cm^2/J	103	Wallace and Kelley 1976
Type III concrete + 40% sludge	94 J/5.80 cm^3	5 impacts 2 kg-0.8 m	0.53	25.3 cm^2/J	136	Wallace and Kelley 1976
SYNROC ceramic + 10% waste						Ramm and Ferenczy 1980
Sintered	127 J/1.53 cm^3	n.r.(b)	2.0	n.r.	n.r.	
Hot-pressed	217 J/1.53 cm^3	n.r.	1.1	n.r.	n.r.	

(a) No <10-µm particles were found.
(b) n.r. = not reported.

3.2 STATIC STRENGTH

Both the tensile and compressive strengths of several waste forms have been measured and reported in the literature.

3.2.1 Tensile Strength

Tensile strength data have been reported for concrete, sintered ceramic, glass ceramic and glass (Wald et al. 1980; Platt 1974; McElroy 1974a,b; Roy and Gouda 1974).

In these tests, small cylinders (1.3 cm dia x 1.3 cm length were compressed (splitting tensile test), and the tensile strengths were derived from the fracture load. These strengths are listed in Table 3.2.

TABLE 3.2. Tensile Strength for Various Waste Forms

Waste Form	Tensile Strength, MPa
Cement + 10% PW-9 calcine powder	8.34
Cement + 10% SPC-5B	7.85
Supercalcine sintered ceramic SPC-5B	28.6
Sintered ceramic 50% frit + 50% PW-9	13.5
Sintered ceramic PW-9	8.80
Hot-pressed sintered ceramic PW-9	13.0
Glass ceramic 20% PW-9	34.3
Glass 76-68	51.4

3.2.2 Compressive Strength

Considerable data have been reported on the compressive strength of various concretes (Savannah River Laboratory 1974a,b,c; Stone 1977; BNL-18978; Berreth et al. 1976; Roy and Gouda 1974; Blanco and Lotts 1979a,b,c,1980; Moore 1979) in which the variations of strength with water/cement ratios, curing time, curing conditions, sludge content, pressure imposed during curing and type of cement were measured. The data are summarized in Table 3.3.

Other studies on concrete cured without pressure show a decrease in normal concrete strength with increasing sludge content from about 62 to 90 MPa at 0% sludge to 10 to 40 MPa at 40% sludge (Stone 1977). Variables reported to have an effect on strength were water/cement ratio (Stone 1977), curing time (SRL 1974c), curing conditions (SRL 1975) and sludge content (SRL 1974a,b,c; SRL 1975; Plodinec 1977; Stone 1977). Sludge content had the strongest effect on strength.

TABLE 3.3. Compression Strength Ranges of FUETAP for Processing and Composition Variations

Waste Forms	Parameter Variations	Strength Range, MPa	Reference
FUETAP 10% simulated waste	Curing temp. 100 to 250°C	20-31	Blanco and Lotts 1979a
FUETAP 10% simulated waste	Pressure 0.1 to 4.1	23-39	Blanco and Lotts 1979b
FUETAP 15% simulated waste	Water/concrete ratio 0.9 to 0.7	26-62	Blanco and Lotts 1980
FUETAP Variable simulated waste content	Waste sludge 10 to 20 wt%	22-28	Blanco and Lotts 1979c
FUETAP 10% simulated waste	Fly ash 7.5 to 27 wt%	6.6-32	Blanco and Lotts 1979c
FUETAP 16% simulated waste	Cement type Type 1	13-14	Moore 1979
	Type 3	14-15	
	High alumina	9	

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4.0 CHEMICAL DURABILITY

J. E. Mendel, J. H. Westsik, Jr., and D. E. Clark

Chemical durability of radioactive waste forms refers to their resistance to reactions with water. Chemical durability is important because radionuclides removed from the waste form by reaction with water can slowly diffuse away from the waste form in static water or be transported away more rapidly if the water is moving. The waste management system is designed to prevent contact of the waste form with water until the waste has remained buried in a geologic repository for hundreds of years, and even then the system will minimize the amount of water that can reach the waste form. However, because water is one of the main potential routes for dispersion of radionuclides from the waste, either in an accident or after long periods in the repository, chemical durability has been a major consideration in the development of radioactive waste forms.

Several reactions can occur between water and radioactive waste forms. The resultant, overall reaction is called "leaching," and the chemical durability of waste forms is determined by measuring "leach rates." Because many different procedures are being used to measure leach rates, comparison of leach-rate data is difficult. Although all the procedures involve contact between water and a waste-form specimen, differences occur in the apparatus, mode of contact, specimen preparation, leachant composition, temperature, pressure, and the thoroughness with which the variables are controlled and documented.

4.1 USES OF CHEMICAL-DURABILITY DATA

Chemical-durability (or leach rate) data serve several purposes; these uses require data of varying rigor. Sometimes data obtained in relatively simple, short-term tests (days) will suffice; at other times the data can be obtained only in detailed, long-term tests (years). The uses of data from leach tests can be divided into three major categories:

I. Waste-form development and characterization

II. Analysis of the safety of waste management systems alternatives (basis for licensing)

III. Quality assurance in a waste-solidification facility.

Most leach testing done to date belongs in Category I. Waste-form developers are using leach rates as a criterion in optimizing their formulations. Category II tests are usually more elaborate than those of Category I and include many components of the repository system. At this time, there are no Category III tests in use since leach testing is not applied as quality control to any waste-solidification facility in the U.S.

4.1.1 Category I Tests: Waste-Form Development and Characterization

Most of the leach testing in waste-form development and characterization programs has used very simple scoping or screening batch tests. These tests usually yield answers in a few days or, at most, a few weeks. Examples of applications of these tests include testing a series of waste-form preparations to determine the effect of varying a waste component, such as sodium, above and below a median concentration, or of testing a series of waste-form specimens of the same composition that have been subjected to increasingly severe thermal or radiation treatments.

4.1.2 Category II Tests: Systems Analysis

Some of the most important scenarios that must be evaluated in risk analyses of nuclear waste management involve water as the transport medium, particularly after the waste is in a geologic repository. The leach rate of the waste form at the conditions of the scenario becomes the source term for the risk evaluation. In these scenarios, leaching behavior is affected by the characteristics of the repository system, which includes the canister, other engineered barriers, the backfill, and the surrounding geologic formations. Systems tests are used to evaluate all of these components. The risk analyses require predictions of leaching behavior that extend far beyond the duration of the leach tests. To do this, the rate-controlling mechanisms should be understood and the test results should be as accurate as possible to minimize the propagation of errors during extrapolation. Because the systems tests are so complex and time-consuming, they are performed only on carefully selected waste forms that represent a range of potential formulations. Simpler auxiliary tests can be used to obtain supportive information.

4.1.3 Category III Tests: Quality Assurance

One of the quality-assurance tests on the product of a radioactive-waste-solidification facility could be a leach test. If so, the test would be a simple, rapid test resembling the comparison tests used in waste-form development. The purpose of the quality-assurance tests would be to quickly confirm that the product of waste solidification is within certain preset leach-rate specifications.

4.2 EXPERIMENTAL DETERMINATION OF CHEMICAL DURABILITY

Experiments to determine the chemical durability of waste forms include three main operations: sample preparation, sample exposure, and analysis. The differences in the leach tests now in use result from selection of different options for one or more of these operations.

4.2.1 Dynamic Leach Tests

Dynamic leach tests are those in which the specimen is exposed to leachant that is either continuously or periodically replenished; i.e., a flow-through system is either employed or simulated. To date, most leach tests have been dynamic.

Recognizing that the numerous different leach tests that were in use made comparison of results difficult, the International Atomic Energy Agency (IAEA) organized a committee to recommend methods for standardizing the leach testing of immobilized radioactive waste solids. A result of these discussions was a suggested standard leach test (Hespe 1971). The main features of the standard test proposed by the IAEA were as follows:

- leachant contact restricted to one surface of the specimen
- ratio of leachant volume (cm^3)/specimen surface area (cm^2) ≤ 10 cm
- temperature = $25° \pm 5°C$

- no agitation of leachant
- leachant replaced daily for 1 week, weekly for 8 weeks, monthly for 6 months, and then twice yearly thereafter
- different leachants permitted, depending on the purpose of the test (for intercomparison, distilled water is used, whereas fluids more typical of the disposal environment are used for hazards evaluations).

The IAEA test has not been adopted widely enough to be useful in interlaboratory comparisons. Many leach tests performed since the proposed IAEA procedure was published are said to utilize "modified" IAEA procedures. Unfortunately, there has been little consistency in the "modifications" adapted at the various laboratories.

Some undesirable features of the proposed IAEA test include the following:

- Canning the sample to expose only one side is an unnecessary complication and is not generally done.
- Changing the water periodically to achieve a dynamic system causes an undesirable "saw-tooth" effect. The concentrations of leached ions build up in the leachant and the pH changes; then the initial conditions are abruptly reinstated when the water is changed and the saw-tooth cycle begins again.

A revised IAEA test has been developed by the International Standards Organization (ISO) and is now being circulated for comment. The ISO Draft International Standard DIS 6961, Long-Term Leach Testing of Radioactive Waste Solidification Products, partially addresses the saw-tooth effect observed in the IAEA test by calling for the addition of pH buffers to the leachant solutions. Testing at three buffered pHs--2.3, 5.7, and 9.5--is proposed to span the range of pH that may occur in natural geologic systems. The ISO test also specifies four experimental temperatures--23, 45, 70, and 100°C--all controlled to ±1°C since variation in temperature significantly affects leach rate. For the draft ISO test the frequency with which leachant is changed differs slightly from that in the IAEA test: daily during the first 5 days; twice during the second week; once a week for the third, fourth, fifth, and sixth week; and monthly thereafter.

The saw-tooth effect associated with the periodic changing of the leachant can be avoided by using a single-pass, flow-through apparatus. The flow can be achieved by use of pumps, head tanks, or Soxhlet-type equipment. A single-pass apparatus using pumps is used at Lawrence Livermore Laboratory (Figure 4.1). Up to 20 samples can be tested simultaneously at flow rates between 13 and 460 cm^3/day in the temperature range of 25 to 75°C (Weed and Jackson 1979).

An example of a single-pass, flow-through apparatus using gravity flow from a head tank is the leaching facility at the Hahn-Meitner Institut in Berlin, which has six units, each capable of holding six samples (Heimerl et al. 1971). Flow rates are variable between 20 and 200 cm^3/week at temperatures controlled between 20 and 50°C.

Soxhlet extractors are a type of single-pass, flow-through leaching equipment. The standard industrial Soxhlet apparatus (Figure 4.2) uses a repetitive siphoning action to ensure that the entire sample is contacted with freshly distilled water. The siphoning occurs frequently (2- to 15-min intervals), so changes in leachant composition due to ions dissolved from the sample are considered insignificant. Some recently devised Soxhlet-like equipment uses direct flow-through without siphoning (Figures 4.3 and 4.4). The main purpose of the recent modifications of the Soxhlet apparatus, however, is to expand the temperature range. Temperatures in the specimen chamber can be controlled from 40 to 99°C.

4.2.2 Static Leach Tests

In static tests the leachant is not replenished, and its composition changes continually as more material is leached from the sample. If static tests are continued long enough, the rate of change in leachant composition may become very low; i.e., it may approach a steady state.

Static tests are simple to perform; however, since they do not represent the worst case (i.e., higher leach rates are obtained in dynamic leach tests), few static leach test data for waste forms are found in the literature. This situation is changing, principally for two reasons. First, there is a growing

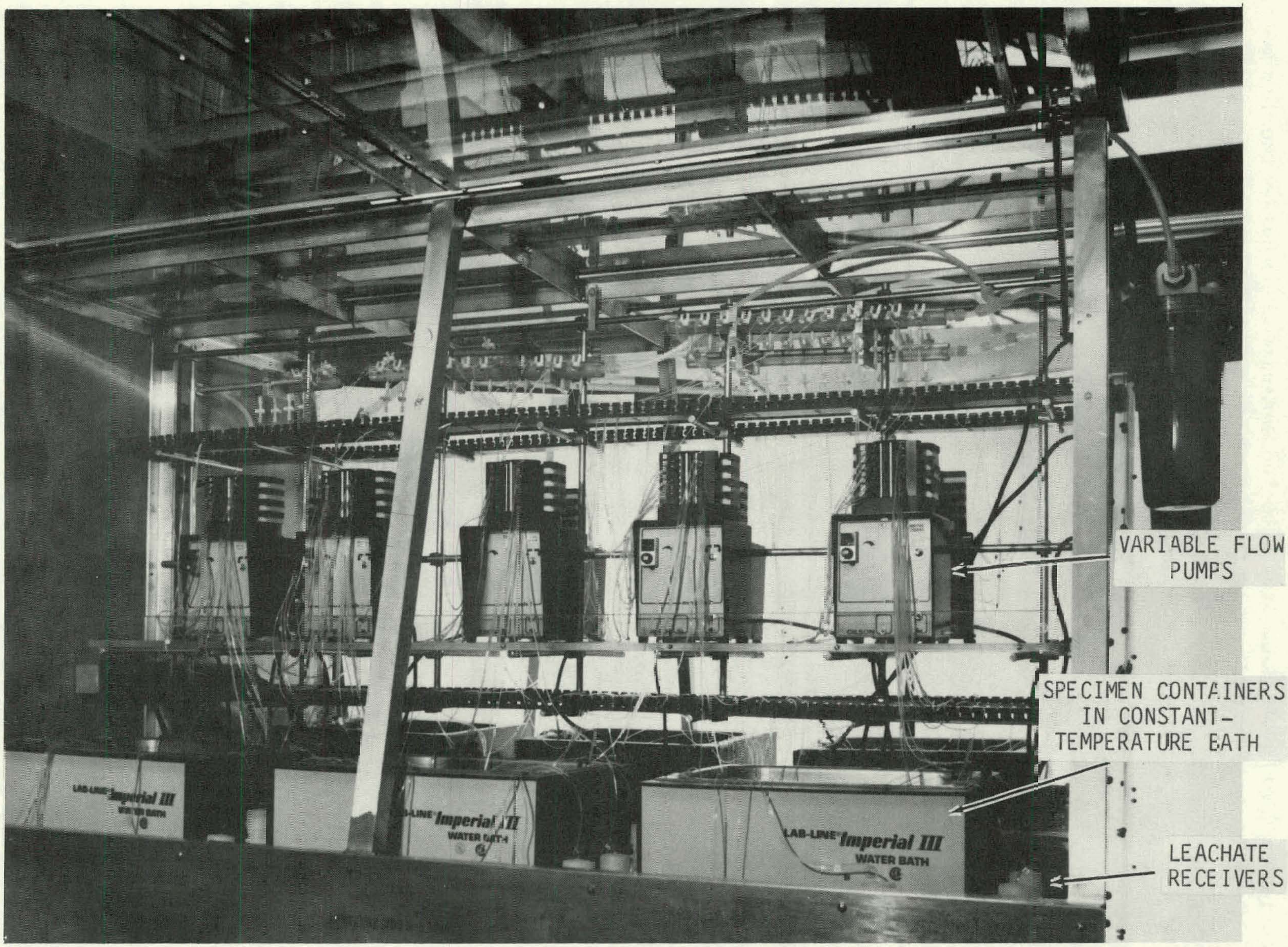

FIGURE 4.1. Lawrence Livermore Laboratory Single-Pass Flow-Through Apparatus

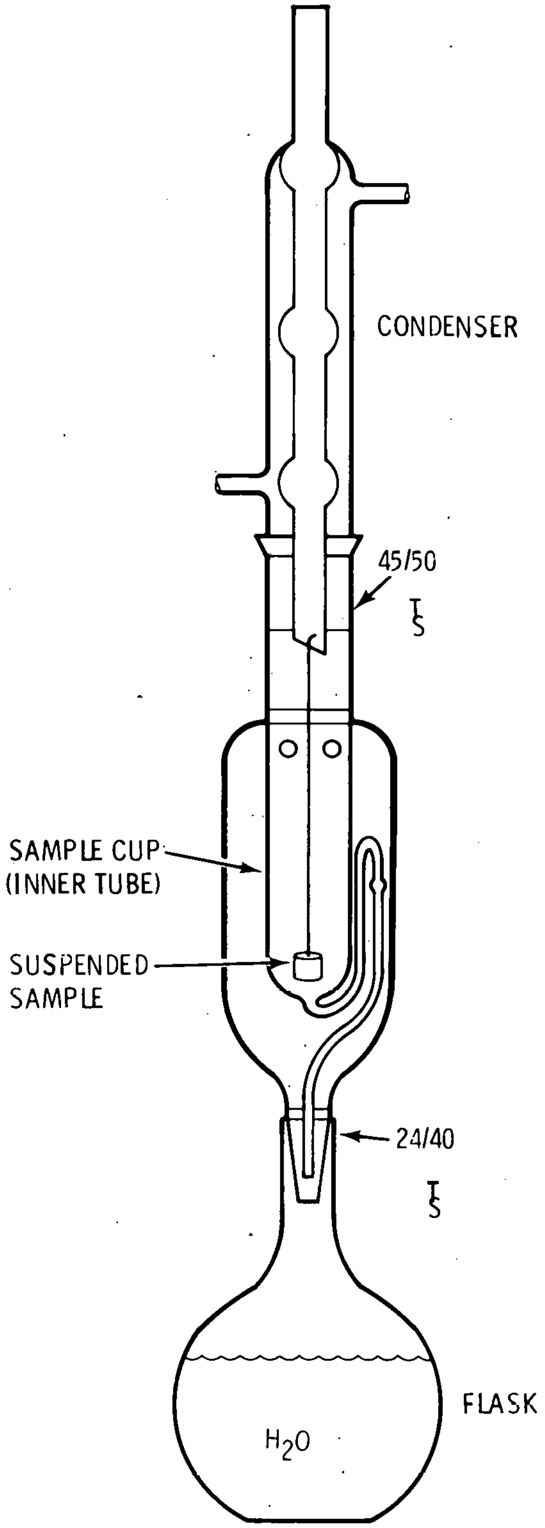

FIGURE 4.2. Representative Industrial Soxhlet Apparatus Adapted for Waste-Form Leaching

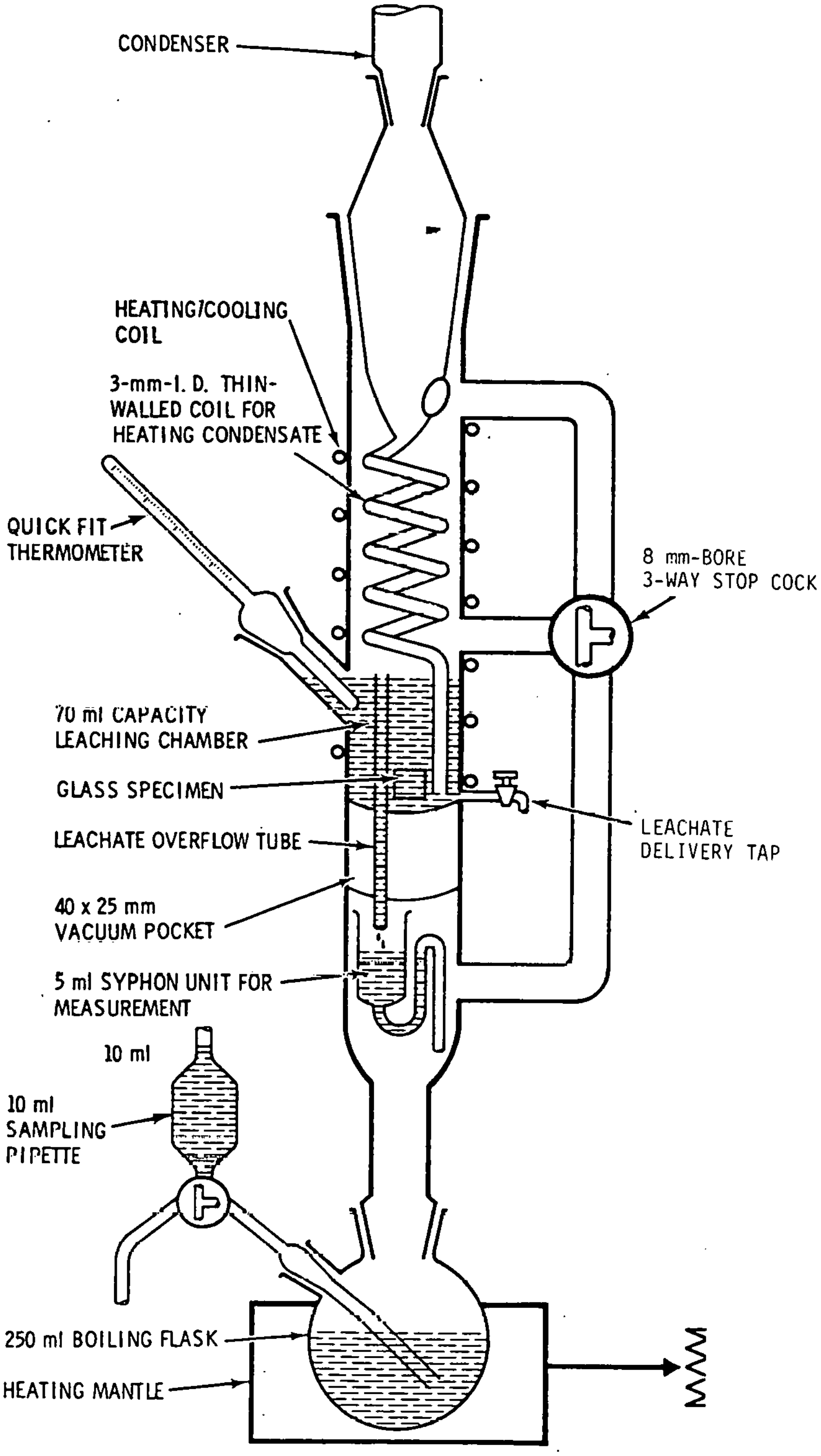

FIGURE 4.3. Soxhlet-Like Apparatus Utilized for Leach Testing in India (adapted from Vaswani 1979)

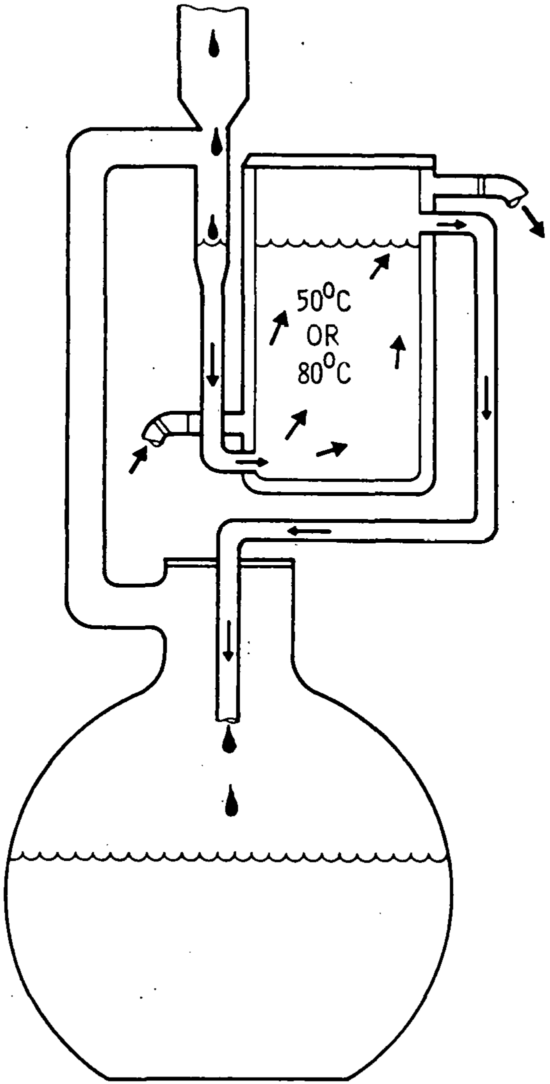

FIGURE 4.4. Soxhlet-Like Leach Test Apparatus Developed at Ispra Research Establishment (adapted from Lanza et al. 1980)

recognition that static leach conditions are realistic for studying many potential, repository-related leaching scenarios, particularly when the multiple barriers of the waste package are considered. Because of these barriers, the flow rate at the surface of any waste form being contacted by water will probably be very low, and the situation can be approximated by static leach testing. Second, some analyses of long-term, waste-water-rock behavior may utilize thermodynamic information. Static tests, particularly those performed at higher temperatures, can help confirm the validity of the thermodynamic assumptions or develop needed new information.

Many of the static leach tests performed to date have been autoclave experiments above 100°C (Bradley et al. 1980; Westsik and Turcotte 1978a; McCarthy et al. 1978; Flynn et al. 1979; and Braithwaite 1979). For waste glasses, steady state is approached in 1 to 3 weeks at 250°C, but at 25°C more than a year is required to reach this condition, even when powdered specimens with high surface area are used.

4.2.3 Waste/Rock Interaction Tests

Waste/rock interactions refer to reactions between the waste form, the backfill and any other special materials, such as sorbent clays, that are included as part of the waste package, and the rock in the surrounding geologic formation. The reactions are more properly termed waste/water/rock interactions, since water is the active transport medium in any reactions that may occur. Water reacts with both rocks and waste forms; the object of the interaction tests is to define the result of the combined reactions.

Waste/rock-interaction tests, which are often termed systems tests, may be either static or dynamic. Static test results are used to define reaction products and the approach of the leachate composition to steady state. Reaction products may precipitate from the solution or form on the surface of the waste form. The internal structure of the waste form can also be changed by the action of water. The alteration can take the form of a hydration rind or, in extreme cases, it can extend throughout the sample. Most static waste/rock interactions are tested in autoclaves at 150 to 350°C to accelerate the reaction rates so that steady state can be achieved within reasonable experimental periods. Gold ampoules are often used to contain the reactants to avoid unwanted reactions with internal autoclave surfaces.

Dynamic waste/rock-interaction tests duplicate repository conditions to varying degrees. The leachant is made up to have the composition of actual site-specific water samples and is pre-equilibrated with crushed rock representative of the repository environment. This "repository water" is then brought into contact with the waste-form sample at a flow rate typical of that which could occur in a repository. As many components of the system can be added to the test simulation as desired. Flow-through autoclave tests that include the canister and downstream rock in the test system are planned for the Waste/Rock Interaction Technology program sponsored by the Office of Nuclear Waste Isolation (Bradley et al. 1980, p. 24). The canister is included in recognition of the fact that it will not disintegrate in a single, one-step event. Instead the corrosion should be nonuniform, and much of the canister will probably remain as a barrier long after it is breached in one or two spots. The test will duplicate this type of canister breach by including an artificial crack (a machined slit) in the canister wall.

In situ tests are another way of characterizing the behavior of the system. Most in situ tests that have been done or are scheduled, however, are designed to obtain structural and heat-transfer information; they are not designed for the study of in situ leach behavior of breached canisters in repositories. An exception is the test program proposed for the Waste Isolation Pilot Plant site by Sandia Laboratories (Sattler et al. 1979).

The Canadian burial experiment in which radioactive glass blocks were buried at Chalk River should be included in any discussion of in situ tests, although the low-temperature, shallow-land burial conditions do differ from the deep geologic repository conditions envisioned for the disposal of high-level waste (Merritt 1977). Perhaps the most important aspect of the Canadian test is not that it is being conducted in situ, but rather that it has continued for over 20 years, a much greater time than any other recorded waste-form leaching experiment. Interestingly, more than 5 years were required to reach steady state.

4.3 METHODS OF EXPRESSING CHEMICAL DURABILITY

Numerous mathematical expressions have been used for reporting the data obtained from testing the chemical durability of radioactive waste forms. These expressions represent different ways of presenting leach rates based on leachate analyses, weight-loss measurements, or specimen-surface analyses. The various expressions are described in detail in this section.

4.3.1 Calculational Techniques for Expressing Leachability

Even as test procedures become standardized, the recommended durability expressions vary from procedure to procedure. This can lead to confusion, and it makes comparison of results difficult. Fortunately, most of the methods of calculating chemical durability can be classified into one of three or four techniques. Simple mathematical relationships tie the techniques together (Godbee and Joy 1974).

Probably the most common technique for expressing chemical durability is as a normalized leach rate. This rate is usually calculated from the following equation:

$$(LR)_i = \left(\frac{A_i}{A_o}\right)\left(\frac{W_o}{SA \cdot t}\right) \tag{1}$$

where

$(LR)_i$ = the leach rate in grams of waste form/cm^2day,[a] normalized to the behavior component "i"
A_i = amount of component "i" that is leached during the time interval t
A_o = the initial amount of component "i" in the waste-form specimen
W_o = the original weight of the waste-form specimen, g
SA = the surface area of the waste-form specimen, cm^2
t = the time interval of leaching, days.

Some confusion can result from the use of the normalized leach rate as calculated in Equation (1). This normalized leach rate has sometimes been called a "bulk" leach rate to ensure that it will not be taken to represent grams of component "i" leached. The assumption made in using Equation (1) is that all of the specimen leaches at the same rate as component "i," i.e., that the leaching is congruent (uniform for all components). In fact, leaching is usually not congruent, leading to the anomaly that the same material can have different "bulk" leach rates, depending upon which component is used for the

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(a) The use of SI units for expressing leach rates has not yet been widely adapted. The data presented in this report will be in terms of the units presently in common use.

calculation. For this reason normalized leach rates calculated by Equation (1) should always be followed by the phrase "based on the behavior of component i" or "normalized to the behavior of component i."

The normalized leach rate can be converted to a penetration rate by dividing the rate by the density of the waste form:

$$PR_i = \frac{(LR)_i}{\rho} = \frac{A_i \cdot V}{A_o \cdot SA \cdot t} \tag{2}$$

where

PR_i = the penetration rate, cm/day
ρ = the density or the waste form, g/cm^3
V = the volume of the waste form sample, cm^3.

The penetration rate is an alternative technique for expressing leaching behavior.

Another useful technique is to express chemical durability either as a cumulative penetration or as a cumulative fraction released. The values are obtained from the following equations:

$$C_{p_i} = \left(\frac{\Sigma A_i}{A_o}\right)\left(\frac{V}{S}\right) \tag{3}$$

and

$$C_{F_i} = \frac{\Sigma A_i}{A_o} \tag{4}$$

where

C_{p_i} = the cumulative penetration based upon the behavior of component "i," implying that the surface of the waste form has been depleted of component "i" to that depth
C_{F_i} = the cumulative fraction of component "i" released
ΣA_i = the cumulative amount of component "i" that has been leached from the waste form.

An additional technique for showing chemical durability is simply to present the concentration of leached ions in solution. This method has become more common since solubility is now recognized as playing a significant role in the interactions between waste form and solution.

Finally, leach rates calculated from simple weight loss determinations have frequently been used, particularly in waste-form-development laboratories. These measurements are inadequate to describe leaching behavior comprehensively; for instance, incongruencies in leaching are not detected.

Because of the variety of expressions being used for chemical durability and interrelationships among the expressions, reports of leaching results should include specimen weight, surface area, volume, and composition. Having this information facilitates conversions among durability expressions so that results of experiments can be readily compared.

One method suggested to make comparisons less difficult is the use of a figure-of-merit, based on the reciprocal of an effective diffusivity coefficient that can be calculated from the first week's data of an IAEA-type test. This approach was suggested by the ANS-16.1 Working Group of the American Nuclear Society (ANS) in drafting the proposed standard, "Measurement of the Leachability of Solidified Low-Level Radioactive Wastes" (Godbee and Compere 1979).

A comparison of leach rates for various waste forms in water is given in Table 4.1. Such tabulations of leach rates are useful for making rough comparisons of waste forms. However, the effects of many important factors must be added to refine data such as are given in Table 4.1. These factors will be discussed in the remainder of this section.

4.3.2 Incongruent Dissolution

Releases of radionuclides from waste forms proceed by the mechanisms of selective leaching and matrix dissolution. Selective or incongruent leaching is typified by faster releases of one or several species in relation to other components of the waste. It results from differences in solubility of different phases in the waste form, from different diffusion rates of mobile ions through the waste-form matrix, etc.

TABLE 4.1. Leach Rates for Various Waste Forms (adapted from Jardine and Steindler 1978)

Waste Form	Leach Rate, $g/(cm^2\text{-day})$	Water Temp. °C	Reference
Pot calcine	10^{-1}	25	Van Geel 1975
Fluid bed calcine	10^{-1}	25	Van Geel 1975
Pot calcine	10^{-2}	25	ARH-2888
Fluid bed calcine	10^{-2}	25	ARH-2888
Cement	10^{-2}-10^{-3}	25	Mendel 1973
Al metal matrix-sintered	3×10^{-3}	25	Berreth 1976
Concrete	10^{-3}	25	Berreth 1975
Al metal matrix-cast	10^{-3}-10^{-4}	25	Berreth 1976
Aqueous silicates (clay)	10^{-4}-10^{-5}	25	Barney 1975
Bottle glass(a)	5×10^{-5}	100	Heimerl 1976
Borosilicate glass	3×10^{-5}	100	Heimerl 1976
Lead matrix(a)	2×10^{-5}	100	Van Geel 1976
Vitromet (63 vol% phosphate/glass 37 vol% lead)	2×10^{-5}	100	Van Geel 1976
Phosphate glass	1×10^{-5}	100	Van Geel 1976
Lead matrix(a)	7×10^{-6}	20	Van Geel 1976
Glass (devitrified)	5×10^{-6}	25	Kelley 1976
Asphalt	4×10^{-6}	25	Mendel 1973
Zn borosilicate glass (devitrified)	2×10^{-6}	25	Mendel 1976
Borosilicate glass (in-can melted)	1.3×10^{-6}	25	Blair 1976
Borosilicate glass	10^{-5}-10^{-7}	25	Van Geel 1975
Phosphate glass	10^{6}-10^{-7}	25	Mendel 1973
Titanates	5×10^{-7}	25	Dosch 1978
Alumina phosphate glass	5×10^{-7}	25	Paige 1966
Phosphate glass	5×10^{-7}	20	Van Geel 1976
Vitromet (63 vol% phosphate glass/ 37 vol% lead)	5×10^{-7}	20	Van Geel 1976
Zn borosilicate glass (as formed)	3×10^{-7}	25	Mendel 1976
Glass (as formed)	2×10^{-7}	25	Kelley 1976
Borosilicate glass	10^{-4}-10^{-7}	25	ERDA-1 1976
Silicate glass (Canadian)	10^{-6}-10^{-7}	25	Mendel 1973
Sintered glass ceramics	10^{-5}-10^{-8}	25	Berreth 1976
Industrial glass(a)	10^{-6}-10^{-7}	25	Mendel 1973
Industrial glass(a)	10^{-5}-10^{-8}	25	Berreth 1976
Silicate melts (fired clay)	10^{-6}-10^{-8}	25	Barney 1975
Silicate glass (U.S.)	2×10^{-7} 6×10^{-7}	25	Mendel 1973

(a) These materials are listed for comparison purposes and contain no simulated waste.

The evidence for incongruent leaching comes from chemical analysis of the leachate and surface analysis of the waste form. Mendel (1973) listed some of the early examples of incongruent leaching, and Table 4.2 contains some recent results of leach tests that also illustrate incongruent dissolution. The alkali and alkaline-earth elements are the most leachable species, with the rare-earth and actinide elements being among the least leachable.

Temperature, solution chemistry, and waste-form composition influence waste-form leaching:

- Westsik and Harvey (1981) have shown that release of the alkaline earths from a waste glass actually decreased as the temperature increased from 150 to 250°C. This decrease in release, apparently associated with solubility effects and secondary phase formation, was sufficient to make calcium, strontium, and barium releases comparable to those of the actinides.
- Both McCarthy et al. (1978) and Westsik and Turcotte (1978b) have reported that dissolution of silicon from glass and from supercalcine was less in salt brine than in deionized water, while releases of the other components to salt brine were higher.
- Hench (1977) has suggested that congruent dissolution of glasses may be caused by a high solution pH.
- Waste-form developers use chemical additives to immobilize specific ions in the solidified waste. The resultant phases may then be less leachable than other parts of the waste form, thus leading to incongruent leaching. For example, Stone (1977) noted that the presence of MnO_2 in a particular sludge composition reduced the leachability of strontium. And Ringwood et al. (1979) modified their SYNROC B in response to the discovery that cesium was segregating into a highly leachable phase.

For the same material, the most leachable elements may be two or more orders of magnitude more leachable than the least leachable. As will be discussed later, most leaching theories predict that, if leaching is continued

TABLE 4.2 Leach Test Results Illustrating Incongruent Dissolution in Deionized Water

Waste Form	Leaching Order	Reference
Glass	Cs>Co,Ag>Zn,Ba>Ru>Zr>Ce,Eu	Flynn et al. 1979
Glass	Cs>Sr,Pu	Plodinec and Wiley 1979
Glass	Na>Si>B>Cs>Sr>Zr>Ce>Tb	Johnson and Marples 1979
Glass	Sr>Cs>α-emitters (actinides)	Rankin and Kelley 1978
Supercalcine	Na>Mo,Rb>Cs,Ba,Ca,Sr	McCarthy et al. 1978
Concrete	Sr>Cs>Pu	Moore et al. 1979
Spent fuel	Cm,Cs,Pu,Ce>Sb,Eu,Sr>U>Ru	Katayama et al. 1980

long enough, it will gradually become congruent; i.e., all elements will leach at the same rate. Tests at room temperature have also experimentally confirmed the trend toward congruency, but, as shown in Table 4.3, have demonstrated that it is a slow trend. The data in Table 4.3 also show that the order of preferential leaching of elements from a waste glass is somewhat influenced by leachant composition.

It is important to understand the leaching behavior of individual radionuclides because risk analyses show that the behavior of some radionuclides is much more important than that of others. Initially ^{90}Sr predominates in importance, but after a few hundred years, during which time the NRC is proposing (CFR 1980) that engineered barriers be designed to prevent any radionuclide release from the repository, the ^{90}Sr will have decayed away. The remaining longer lived radionuclides can then be ranked in order of importance. When this is done, ^{99}Tc is usually found to be the most important. For example, Barney and Wood (1980) report the ten most important radionuclides in a basalt repository are, in order of decreasing hazard, ^{99}Tc, ^{129}I, ^{237}Np, ^{226}Ra, ^{107}Pd, ^{230}Th, ^{210}Pb, ^{126}Sn, ^{79}Se, and ^{242}Pu. The leaching behavior of ^{99}Tc from waste glass is anomalous. Its rate of release is initially higher than for any other element, but as leaching continues, the rate

TABLE 4.3. Leach Test Results Illustrating Incongruent Dissolution of Actinides as a Function of Leachant and Time (adapted from Bradley et al. 1979)

Element	Observed Ranking of Element Release from Highest to Lowest Element Release	Ratio of Highest to Lowest Element Release at Time - 1 Day	Ratio of Highest to Lowest Element Release at End of Leach Time(a)
WIPP Brine	Np, Am, U, Pu, Cm	36	20
$CaCl_2$	Am, Cm, Pu, Np, U	7	5
NaCl	Np, Am, Cm, Pu, U	18	10
$NaHCO_3$	Np, U, Am, Pu, Cm	12	3
Deionized water	Np, Cm, Pu, Am, U	37	11

(a) Leach times varied from 40 to 600 days.

drops rapidly until it is lower than those of most of the actinides (Bradley et al. 1979). This behavior is believed to result from technetium's being phase-separated in tiny, very leachable globules in the glass matrix.

These are just a few examples of the influence of temperature, waste-form composition, and leachant-solution composition on incongruent leaching. The following sections provide more detailed discussion.

4.3.3 Correlation of Incongruent Dissolution with Surface Analyses

While solution analyses are most frequently used as evidence for incongruent leaching, surface analyses are also useful. The techniques used to study leached surfaces range from simple optical examination of polished cross sections to instrumental methods employing sophisticated equipment. The results verify that incongruent leaching occurs, but also suggest that solubility, structural alterations, and reprecipitation complicate the leaching process.

Of the many techniques available for examining leached surfaces of waste forms, the simplest methods are visual examination and optical microscopy. Scanning electron microscopy (SEM) with energy-dispersive analysis by x-ray (EDAX) is frequently used to supply compositional information about the surface. Other instrumental techniques are also available for surface analyses and can be categorized according to the depths of surface analyses achieved. Table 4.4, taken from Hench (1977), lists most of the surface analysis techniques available for examining radioactive waste forms.

Most frequently, surface analysis is used to establish concentration profiles of elements within the leached layer of the waste form. This information can be used in developing or validating models for the leaching process. Short-time, low-temperature leach tests yield reaction layers thin enough (5-20 Å) to be examined by outer surface methods. Clark et al. (1979) used Auger spectroscopy and infrared reflection spectroscopy to show that a nuclear waste glass underwent material loss from combined selective leaching and matrix corrosion. Figure 4.5 shows typical profiles illustrating incongruent dissolution. The schematic drawing in Figure 4.6 of the leached layer of another waste glass was prepared by Houser et al. (1978), who used sputter-induced optical emission to determine that boron, the alkali metals, and the alkaline earths were diffusing from the glass surface. A barrier layer was formed that contained mainly the transition metals but no silicon. An outer reactive layer containing silicon and enriched in the rare earths was also observed.

As the duration or temperature of the leach test increases, the thickness of the reaction layer increases beyond the analytical capabilities of the near-surface analysis techniques. Electron-beam microprobe and SEM-EDAX systems are used to examine cross sections of these thicker layers. Kenna and Murphy (1979) examined the surfaces of a sodium titanate ceramic and a waste glass that had been leached 20 months in a Soxhlet apparatus. Microprobe analyses did not reveal any reaction layer on the ceramic. The glass did exhibit a leached layer, and the authors postulated that a diffusion barrier had formed within the leached layer, since normally mobile sodium, iron, zinc, and phosphorus had concentrated in zones within the reaction layer.

High-temperature leaching by salt brine also results in the formation of leached layers both in waste glass and in supercalcine. Westsik and Turcotte (1978b) used SEM-EDAX to examine the leached layers formed on PNL 76-68 waste

TABLE 4.4 Instrumental Techniques for Analyzing Glass Surface[a]

Methods	Depth of Analysis
Electron Spectroscopy for Chemical Analysis (ESCA)	5-20 Å
Auger Electron Spectroscopy	5-20 Å
Ion-Scattering Spectroscopy	5-20 Å
Secondary Ion Mass Spectroscopy	5-20 Å
Ion-Beam Induced Radiation	5-20 Å
Ar Ion Beam Milling with the above techniques	5-2000 Å
Ellipsometry	<10->1000 Å
Infrared Reflection Spectroscopy	0.2-0.5 μm (2000-5000 Å)
Electron Beam Microprobe	1.5 μm
Scanning Electron Microscopy (SEM) - with Energy-Dispersive Analysis by x-ray (EDAX)	1.5 μm
Surface Dielectric Analysis	~1-10 μm
X-ray Fluorescence Spectroscopy	10 μm

(a) Adapted from Hench 1977.

glass and supercalcine SPC-4. Their study showed that the mobility of ions and alteration of the glass surface depend on the composition of the leachant. Figure 4.7 shows the cesium-concentration profile across the reaction layer on the supercalcine specimen.

The scanning electron microscope and the microprobe have also been used to determine which phases in a composite waste form are more durable. Rankin and Kelley (1978) and Wald and Westsik (1979) reported that in devitrified glasses the residual glass matrix leaches faster than the crystalline phases that formed.

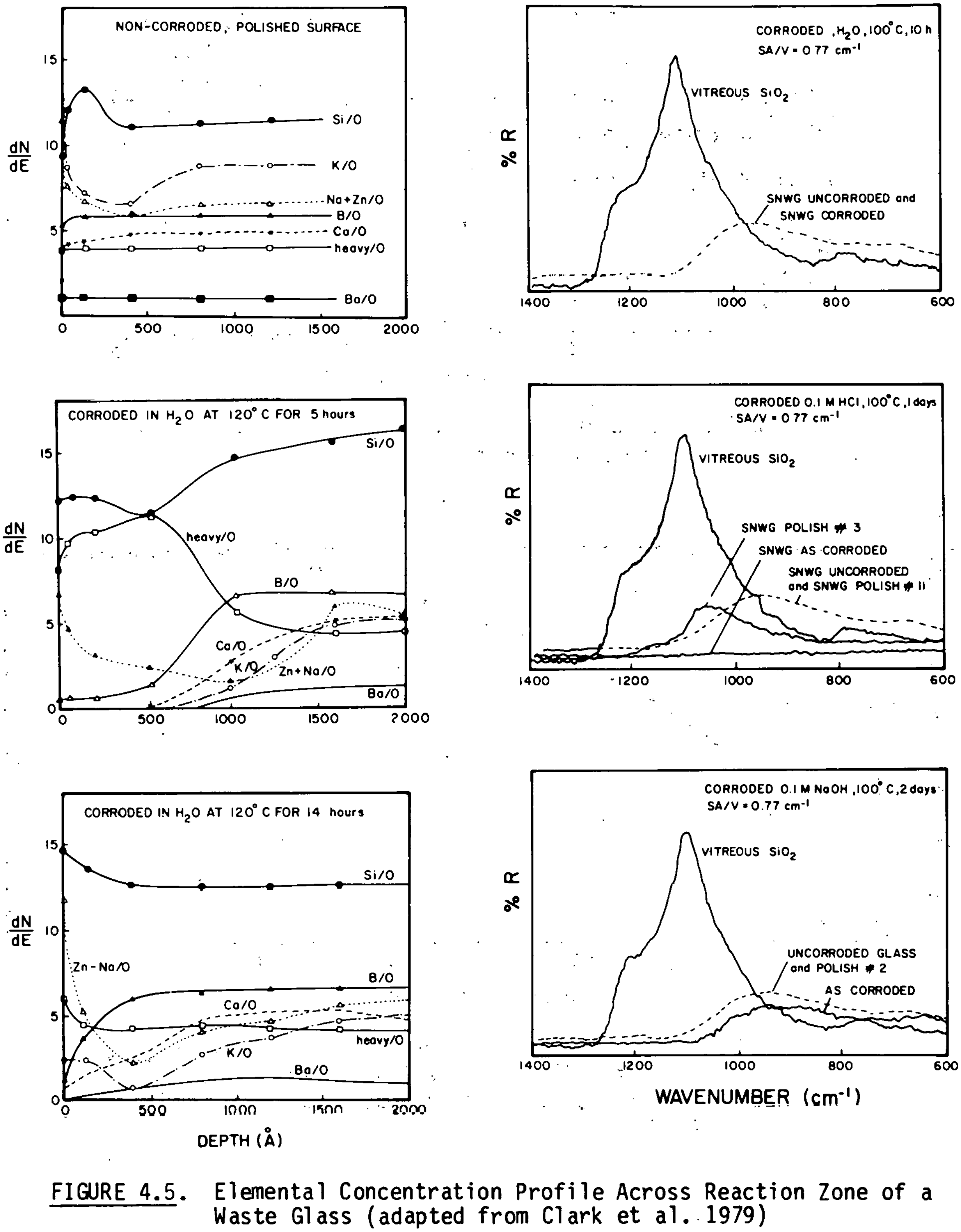

FIGURE 4.5. Elemental Concentration Profile Across Reaction Zone of a Waste Glass (adapted from Clark et al. 1979)

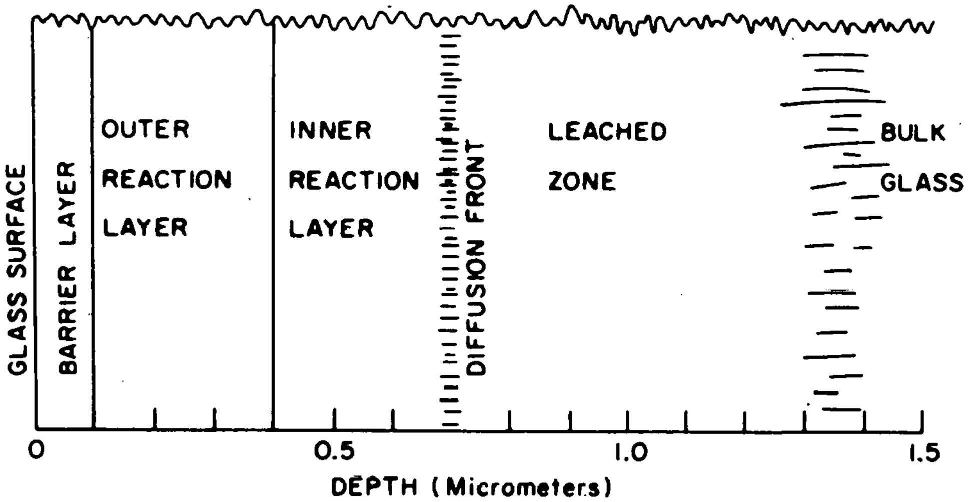

FIGURE 4.6. Schematic of Leached Layer of a Waste Glass (adapted from Houser et al. 1978)

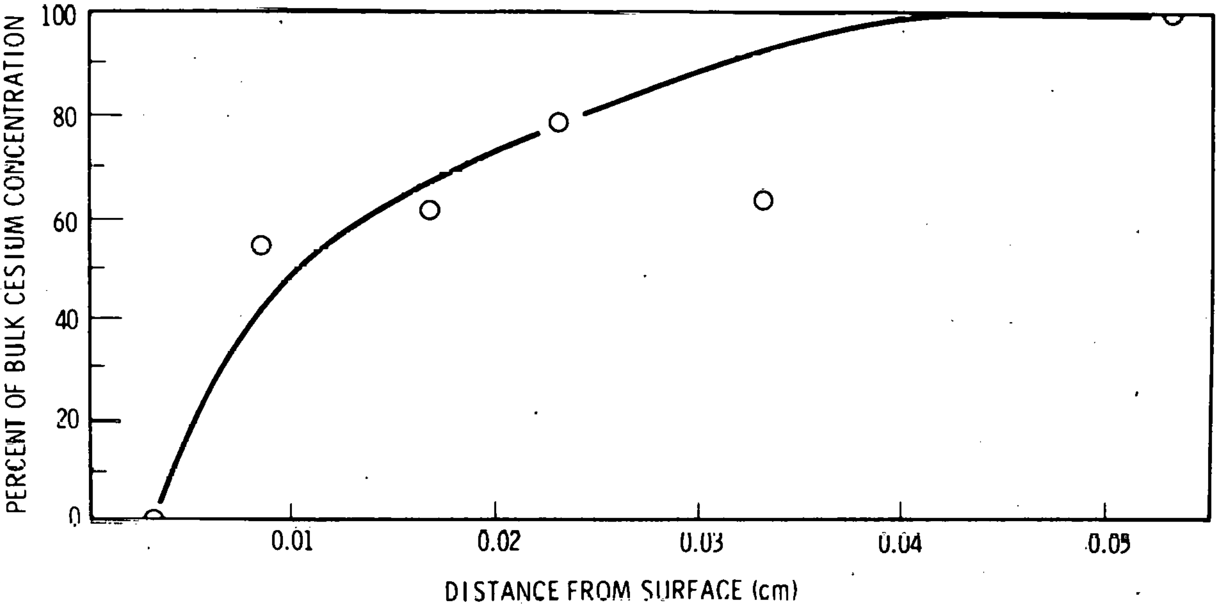

FIGURE 4.7. Cesium-Concentration Profile Across the Reaction Zone of a Supercalcine Pellet After Leaching in Salt Brine (adapted from Westsik and Turcotte 1978a)

4.4 EFFECT OF TEMPERATURE

When a waste form is initially confined in a geologic repository, the heat-producing characteristics of the waste increase temperatures and establish temperature gradients. Pressures as high as 2500 psi will exist at the repository depths presently being contemplated (>1000 m). Therefore, leaching studies spanning the entire range of the geologic-burial conditions are required (i.e., elevated temperature, radiation fields, high pressures, etc.) to judge the potential for radionuclide releases from the waste. Unfortunately, attempts to study leaching under these conditions may be complicated by changes in the leaching mechanisms. Under geologic conditions, the waste form itself may undergo changes (hydrothermal transformations) that significantly affect the leach rates. Thus correlations of test results with geologic conditions are very complex and difficult.

4.4.1 Expected Temperatures

The actual self-heating temperature of the solid, radioactive waste form will depend on factors such as

- waste loading
- age of the waste
- constituents of the waste
- shape and size of the waste form
- thermal properties of the waste form
- thermal properties of the surroundings.

The heat-generation rates for high-level waste decrease rapidly with time out of the reactor; e.g., 18.5 kW/MTU at 160 days decreases to 0.86 kW/MTU at 10 years out of the reactor (ERDA-76-43, Vol. 2, 1976). In the conceptual treatment of high-level wastes, the solidified waste form (e.g., glass) is contained in a waste canister (e.g., stainless steel) 150 to 610 mm in diameter and 0.6 to 4.5 m in length (ERDA-76-43, Vol. 3, 1976). The projected loading of such a canister could result in an initial heat-generation rate of as much as 13 kW. The heat generation will decrease during interim surface storage. However, the actual waste loading may be determined by the upper limits acceptable for the waste-form surface temperature in the repository. What the acceptable maximum allowable temperature will be is still under study; it may be 100 to 150°C.

4.4.2 Effects of Temperature on Leaching

The overall dissolution processes are expected to exhibit complex temperature dependences due to the many interactions involved and changes in mechanism with temperature. Studies of leaching behavior at different temperatures permit the prediction of leach rates as functions of temperature, assuming Arrhenius-type relationships. However, the apparent activation energy calculated from an Arrhenius expression applies only to a given reaction mechanism and should not be used for extrapolation to different reaction conditions.

Lanza and coworkers (1980) have studied the water leaching for borosilicate glass and found that a good fit of the weight loss versus time data was obtained by the expression

$$\text{Weight loss} = a\ t^{1/2} + b\ t$$

where a and b are constants and t is the time. The corresponding rate expression is given by

$$\text{Rate} = \frac{1}{2}\ a\ t^{-1/2} + b$$

for times up to about 8000 hr. At 50°C, $a = 1.0 \times 10^{-4}$ and $b = 5.7 \times 10^{-7}$; at 80°C, $a = 2.5 \times 10^{-4}$ and $b = 3.6 \times 10^{-6}$. Using these data, apparent activation energies can be calculated from an Arrhenius-type relationship, and calculated results for different times are given in Table 4.5. For short exposure times, when diffusion is presumed to be the dominant mechanism (with a square root of time dependence), the apparent activation energy, E_{act}, is ~6.9 kcal/mole. After long exposure times, when corrosion is assumed to predominate, the rate becomes independent of time and the apparent E_{act} approaches 13.9 kcal/mole.

TABLE 4.5. Apparent Activation Energy for Leaching of Borosilicate Glass by Water as a Function of Exposure Times at 50 and 80°C

Exposure Time, hr	Apparent E_{act}, kcal/mole
0	6.92
100	8.01
1000	8.48
8000	11.23
∞	13.93

The general trend of reported temperature effects shows that a factor of 10 to 100 increase in leaching rate from ambient temperature to 100°C is typical and indicates the importance of temperature control in leaching experiments.

Adams (1979) studied the leaching of simulated nuclear waste glasses of a sodium-borosilicate type (glass Q) with a low waste loading and of a zinc-borosilicate type (glass R) with a high-waste loading. The leach depth (LD) was calculated for each test specimen based on the sodium extraction; fitting of the data was done with the expression:

$$LD = A \sqrt{t}\, e^{-E_{act}/RT}.$$

Some of the results for 20-week rates are shown in Figure 4.8 for cases of significant and limited reaction-product buildup (RPB). The activation energies for the reactions of the two nuclear waste glasses with distilled water were found to be ~20 kcal/mole, or about the same as those found for ordinary commercial glasses, but may decrease to ~10 kcal/mole when significant reaction products are present.

Boult and coworkers (1979) have reported on long-term (up to 11 wk) Soxhlet tests and flowing-water tests on glass compositions proposed for waste vitrification in the United Kingdom. Their results, based on weight losses, are shown in Figures 4.9 and 4.10 as Arrhenius plots; for comparison, lines corresponding to activation energies of 15 and 22 kcal/mole are included.

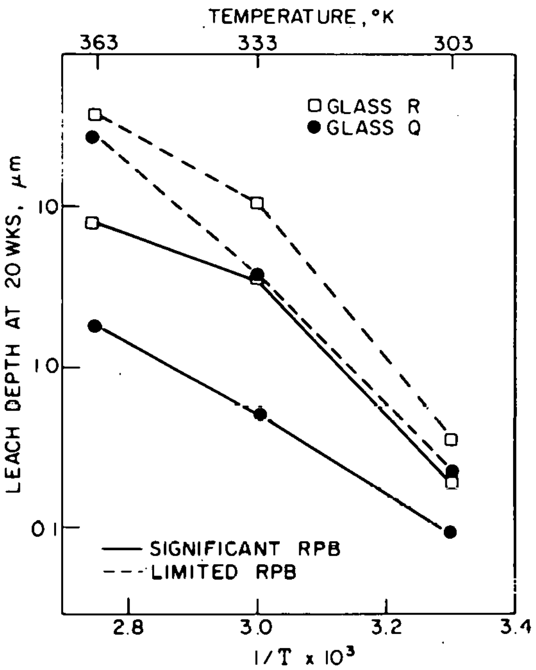

FIGURE 4.8. Relevance of Sodium Leaching Data to the Arrhenius Expression (adapted from Adams 1979)

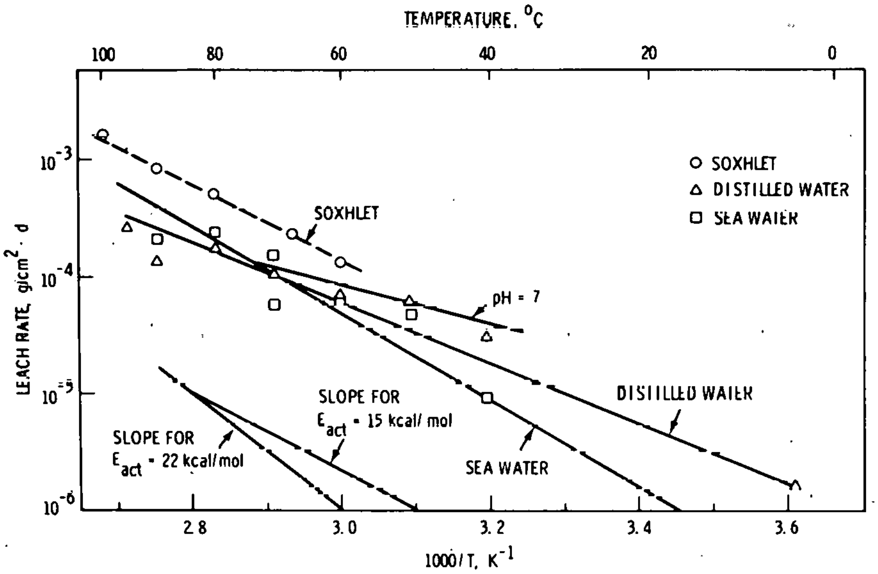

FIGURE 4.9. Soxhlet and Static-Water Leach Rates for Glass 189 (adapted from Boult et al. 1979). The Soxhlet results for temperatures below 100°C were obtained by boiling the water under reduced pressure. The leach rates in flowing water (pH = 7) are included for comparison.

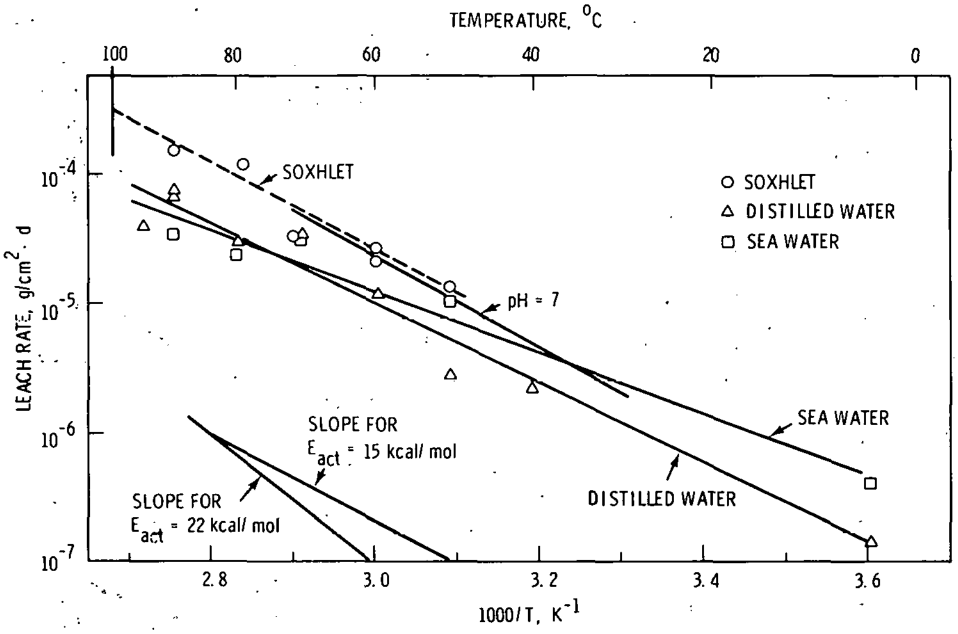

FIGURE 4.10. Soxhlet and Static-Water Leach Rates for Glass 209 (adapted from Boult et al. 1979). The vertical line at 100°C shows the spread of 11 different Soxhlet results.

These workers also measured the effect of pH on leach rates at different temperatures as shown in Figure 4.11. The leach rates are increased at lower pH values.

Temperature studies on FINGAL borosilicate glass were performed by Elliot and Auty (1967) using radiotracers. Crushed-glass specimens were leached by a once-through method. The large temperature coefficients that were obtained corresponded to activation energies of about 12 to 20 kcal/mole. Borosilicate glasses were shown to be more durable than a phosphate glass by a factor of ~5 to 10.

The leachability of simulated, vitrified, high-level waste was tested up to 300°C by Japanese workers (Amano 1979) using a high-pressure, Soxhlet leachability-testing device. Granules, ranging from 35 to 60 mesh, were tested for 2 hr at the ratio of 6 g to 300 ml of distilled water. The leach rates based on cesium were 6.5×10^{-6} and 1.3×10^{-4} g/cm^{-2}·d^{-1} at 100 and 295°C, respectively. Although sodium was leached at about the same rate as

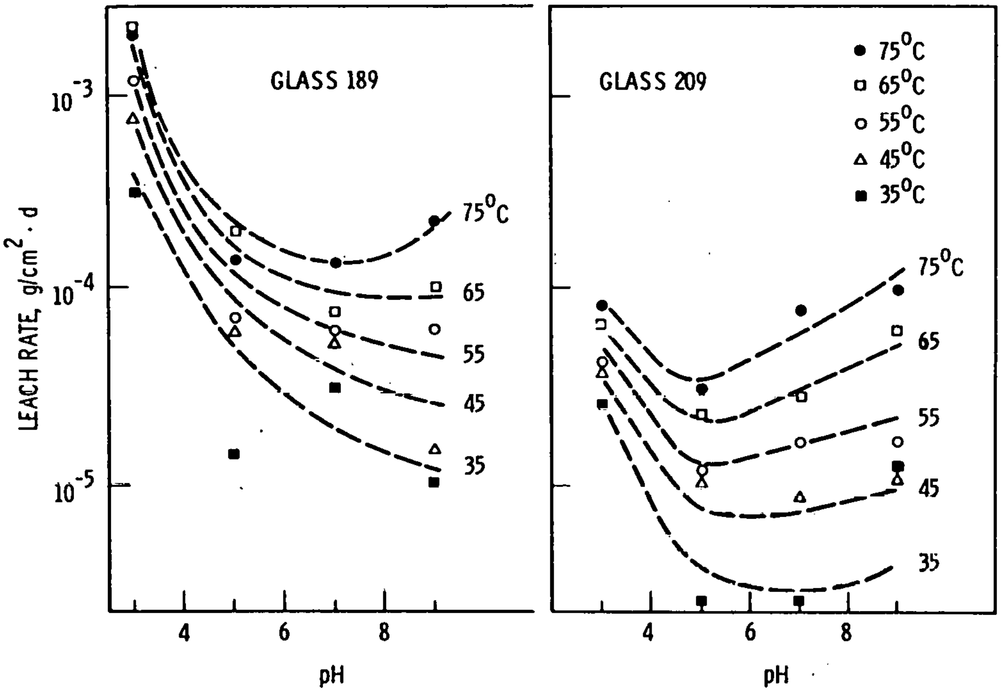

FIGURE 4.11. The Effect of pH on Leach Rate of Glasses 189 and 209 at Different Temperatures (adapted from Boult et al. 1979)

cesium at 100°C, its temperature coefficient was less (E_{act} ~7.8 kcal/mole for cesium and ~4.6 kcal/mole for sodium), so that the 295°C rate is approximately one-fourth that for cesium. The results are comparable to those for leaching of ^{137}Cs from cement composites (Emura 1974), in which E_{act} was determined to be about 4 to 5 kcal/mole.

4.4.3 Hydrothermal Reactions and Their Impact on Leaching Behavior

After a repository is sealed, the potential exists for hydrothermal reactions (reactions with water under pressure at temperatures >100°C). The potential for the reactions cannot exist unless several precursor events occur concurrently: 1) the emplaced waste must contain enough self heat to raise the temperature above 100°C, 2) water must be present, 3) the repository system must be sealed so that the water does not escape as steam, and 4) the hard barriers in the waste package , i.e., the canister and overpack, must fail so rapidly that the water will still be above 100°C when it contacts the waste form. Studies of the stability of potential waste forms such as borosilicate glass have been conducted under hydrothermal conditions, and significant alterations, including devitrification, have been reported (McCarthy 1979, McCarthy 1978, U.S. DOE 1980, and Braithwaite 1979). Waste/rock interactions at elevated temperatures and pressures, in the presence of water, may be accelerated over those same interactions at room temperature. The phenomenon needs much greater study in order to reliably predict long-term behavior and durability of the potential waste forms being considered.

Long-term, elevated-temperature leaching of simulated waste glass and ceramic materials was performed by Kenna and coworkers (1978) at Sandia Laboratories. They reported a periodic process in which maximum and minimum leaching rates are obtained cyclically; this effect appears to be due to surface roughening followed by formation of a surface film that loses its integrity and sloughs off. The formation of surface films that would periodically slough off was also reported by Dosch (1979) in the 95°C Soxhlet leaching of zinc-borosilicate glass loaded with simulated waste oxides. By contrast, the appearance of a titanate ceramic waste form remained unchanged. In leaching studies with monolithic samples at 250°C in distilled water, salt brine, and sea water, the attack on both forms was more severe at the higher temperature, and formation of surface films subject to sloughing off was observed with the glass.

Table 4.6 compares preliminary leach data for three waste forms (SYNROC-B, supercalcine SPC-4, and borosilicate glass) in deionized water at three temperatures (150, 250 and 350°C)

Leaching of simulated high-level waste glasses, a supercalcine, and a natural glass was studied over the temperature range of 250 to 350°C (Westsik and Turcotte 1978a). A grouping of elemental releases, somewhat independent of waste form, was observed. Some elements (e.g., alkalis) exhibited an increase in release rate with temperature, while others (e.g., calcium, strontium, and iron) showed a leach-rate decrease as temperature increased. This behavior is related to individual chemical properties, changes in solution properties, and possible secondary reactions. Measurable changes also occurred when the waste

TABLE 4.6 Comparison of Preliminary Leach Data for SYNROC, Supercalcine SPC-4, and PNL 72-68 Glass in Deionized Water (adapted from Cornman 1980)

	Fraction Leached/cm^2 x 10^4 at 2000 psi								
	Synroc B			SPC-4			PNL-72-68		
Element	105°C	250°C	350°C	150°C	250°C	350°C	150°C	250°C	350°C
Cs	220	350	430	7.3	15	9.8	8	29	450
Na	126	215	224	8.2	13	12	10	58	1500
Mo	50	50	70	7	13	12	4	52	1100
Ba	0.53	0.18	0.18	--	--	--	1.6	0.99	1.2
Sr	0.35	0.14	0.12	0.85	0.88	0.58	2.3	3.5	3.6
La	0.05	0.08	0.32	--	--	--	--	--	--
Al	7.2	15.9	20.3	6.6	19	12	--	--	--
Zn	13.1	4.7	0.6	--	--	--	--	--	0.14
Ni	6.5	12.6	0.1	--	--	--	--	--	--
Si	--	--	--	24	38	52	7.5	22	150
Fe	2.8	3.7	0.7	--	--	--	0.16	0.56	1.9

solids were contacted with salt brine at temperatures of 250 and 350°C. Thus glass is converted to a mixture of crystalline phases (i.e., undergoes devitrification) within exposure periods of a few weeks. These studies indicate that virtually all solid materials show hydrothermal reactivity at 250 to 350°C, making such elevated temperatures undesirable for containment of radioactivity.

At Sandia Laboratories, the durability of a simulated copper-borosilicate waste glass and titanate waste ceramic under hydrothermal conditions have been studied (Braithwaite 1979, Braithwaite and Johnstone 1979). The major factors affecting matrix stability and cation leachability were found to be solution composition, pH, temperature, particle size, time, and solution saturation and equilibrium. Significant hydrothermal effects were observed, indicating that these conditions need to be considered and controlled if the waste form is to be an effective barrier to release.

Workers at Argonne National Laboratory (Flynn, Jardine, and Steindler 1979, Steindler et al. 1980) have investigated high-temperature leaching behavior of waste glass and canister materials. Significant differences in the temperature dependence of leach rates of different elements were observed (e.g., a waste form unsuitable for cesium at high temperatures was not necessarily unsuitable for actinides).

Studies at Pennsylvania State University have been conducted on hydrothermal reactions of simulated high-level waste glass with water at 300°C (McCarthy et al. 1980). Extensive reaction occurred within a few weeks, resulting in devitrification of the glass, dissolution and transport, and recrystallization of some of the constituents. McCarthy and coworkers (1979) have also considered waste/rock interactions in studying the stability of waste forms in repository environments.

4.5 EFFECT OF LEACHANT COMPOSITION

When considering potential leaching scenarios for nuclear waste forms, a broad range of leachant compositions is possible. The fluids potentially contacting the waste form include the clean water of an interim storage basin, where the impurities are maintained at very low levels, the "rock soup" of a wet, waste-heated repository, where the impurities may reach 100,000 ppm (or even higher in a salt repository), and many intermediate compositions. This wide range of potential leachants creates the need for site- and scenario-specific leach tests. These tests will be conducted when the sites and scenarios are better defined. Meanwhile, many leach tests are being conducted using either generic compositions or deionized water as the leachant.

4.5.1 Effect of pH

The pH of natural waters ranges between 2 and 10; most ground water, however, lies in the more restricted pH range of 5.5 to 8 (Wedepohl 1967). The pH of sea water is uniformly 8 to 8.4. Increased temperature lowers pH because the ionization of water increases with temperature. It has also been reported that the pH of the leachant can be lowered in radiation fields (Rai et al. 1980). Various pH values have been reported for potential repository waters, ranging from pH 3 for hot salt brine to pH 10 for basalt and granite fluids.

Leaching of most waste forms is increased at both high and low pH and is minimum at pH 6 to 8. The leaching behavior of waste glasses as a function of pH is well documented; little information is available concerning pH effects on alternative waste forms, but some deductions can be made by analogy with non-waste-containing crystalline materials.

Figure 4.12 shows the leaching behavior of several waste-glass compositions as a function of pH. For comparison, the relative effect of pH on rate of attack on ordinary commercial container glass is shown in Figure 4.13.

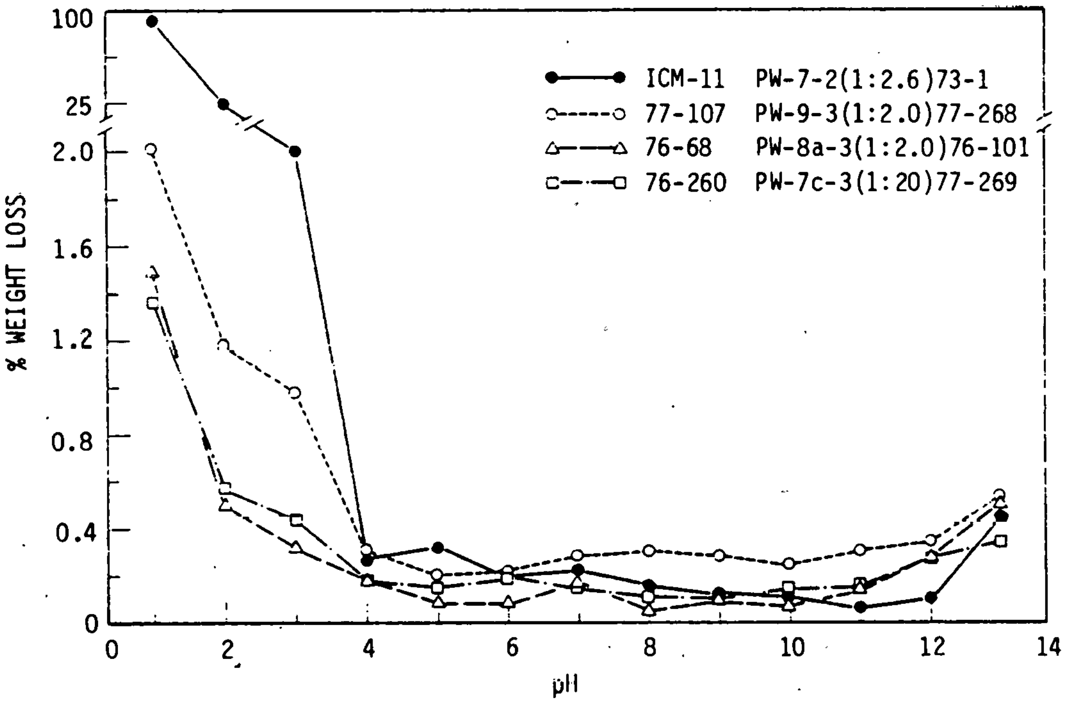

FIGURE 4.12. Effect of pH on Leaching Behavior of Typical Borosilicate Waste Glasses (adapted from Ross et al. 1978)

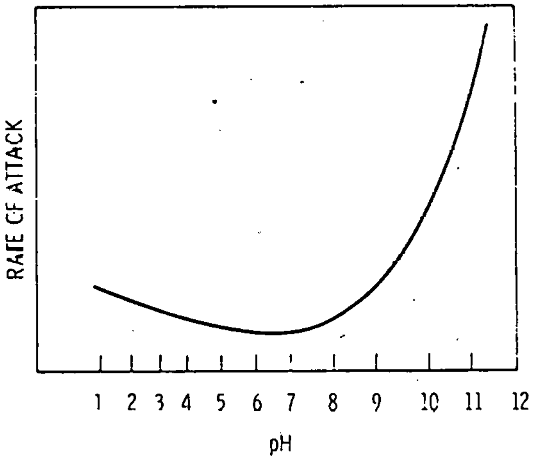

FIGURE 4.13. Effect of pH on Leaching of Commercial Container Glass (adapted from Adams 1972)

Both figures illustrate that the minimum leach rate occurs around neutral conditions, and they also illustrate various differences that exist between waste and commercial glasses. Because of compositional differences, a low pH has the greater effect on the leaching of waste glass, whereas a high pH has the greater effect on the leaching of commercial glass. Waste glasses usually contain less than 50 wt% SiO_2; commercial container glasses contain more than 70 wt% SiO_2. This accounts for the difference in behavior at low pH. Behavior differences at high pH are probably related to the relatively high quantities of transition, rare earth, and actinide elements in the waste glass, most of which are insoluble in basic solutions.

Attack in acid solutions is mainly due to the exchange of hydrogen ions for cations in the glass matrix. The attack would be expected to increase with increasing acidity; however, in high-silica glasses the matrix remains relatively intact, thus impeding movement of the ions. In waste glasses, which normally have a lower silica content, more acid-soluble species are in the matrix, and these glasses exhibit poorer durability in acid solutions. However, as shown in Figure 4.12, the pH must be less than 4 before a significant increase in leach rate occurs.

The stability of naturally occurring minerals varies under acid attack. Some minerals, such as quartz and zircon, are very insoluble in acids. Others may partially dissolve, leaving a siliceous framework, or even become totally gelatinous (Carroll 1970, p. 101). Data on the pH dependency of water attack on several minerals can be found in the following references: Grandstaff 1977, Luce et al. 1972, Siever and Woodford 1979, White and Claassen 1979, and Wollast 1967. In all cases, the rate of attack increases as the pH decreases. The highest pH studied in these references was 9.6, which corresponded to the lowest rate of attack. Waste glasses also exhibit low rates of attack at pH 9.6 and even well beyond pH 10, the extreme occurring in nature (see Figure 4.12). In contrast, the attack on commercial container glass begins to accelerate at about pH 8.

Mechanisms postulated as responsible for alkaline attack on silicate glasses include 1) the increased solubility of silica in alkaline solutions due to formation of $HSiO_3^-$ ions and 2) the direct OH^- attack on silica in the glass matrix. Even fused silica and quartz are attacked, beginning at about pH 9. But the attack on at least some waste glasses remains low up to pH 11 and on some minerals to at least pH 9.7. Apparently certain constituents in these materials hydrate on the surface and form a barrier that impedes attack on the silica matrix. Zirconium, for instance, is added to commercial glasses for applications where a very high alkaline durability is desired (Paul 1977). The rare earths, iron, titanium, and some of the actinides should also provide alkaline protection.

Experimentally the pH dependence of leach rates has usually been determined by adding mineral acids or bases, or by using buffers, to achieve the desired pH. Unless buffers are used, some changes in pH will occur during the course of the experiment. This can be counteracted by adding an automatic pH titrator filled with mineral acid to the experiment for pH control. If a buffer solution is used, care must be taken to ensure that the leach rate is not influenced by complexing or other reactions due to specific buffer constituents. For instance, acetate has been found to greatly increase the leach rate of waste glass (Ross et al. 1978).

4.5.2 Effect of Eh

The oxidation potential of ground water, usually expressed as Eh, generally decreases with depth in the earth. At proposed repository depths of 300 to 1000 m, potential leaching conditions are expected to be highly reducing. Oxygen from the air will, of course, be introduced during repository mining and operation, but some proposed repository locations contain sufficient S^{-2}, Fe^{+2}, etc., to rapidly re-establish reducing conditions following repository closure.

The leach rate of any element that readily exists in more than one valence state can conceivably be influenced by the Eh of the leaching solution. Important waste radionuclides that fall in this category are ^{99}Tc and all the actinides except probably curium and americium.

The oxidation potential becomes especially important in the leaching of spent fuel, for which most of the leach testing under reducing conditions has been done. Otherwise, nearly all the leach test data reported in the literature have been obtained in air-saturated solutions. The Eh is not usually reported, but it may be assumed to be in the range +0.4 to +0.8.

Uranium is more mobile in the hexavalent state. Therefore, leach tests of spent fuel in which air oxidation of UO_2 can occur may yield leach rates that overestimate the rates in a repository situation. For this reason, Norris (1979) leached spent fuel under reducing conditions. He reported lower leach rates for several spent-fuel constituents when reducing conditions were employed. Cesium was an exception; its leach rate was apparently independent of Eh.

Measurement of Eh is difficult (Brandstetter et al. 1979). Leach tests in which Eh can be controlled and known quantitatively are currently being designed, but as yet none has attained widespread acceptance. Use of a glove box with an inert or reducing atmosphere may be desirable. Norris (1979) adjusted Eh by purging his apparatus with a mixture of hydrogen and argon. Other workers are investigating the use of quinhydrone, or pre-equilibration of the leachant with iron (II) compounds.

4.5.3 Cations and Silica in Leachant

The major cations present in natural waters are Na^+, K^+, Ca^{+2} and Mg^{+2}. Appreciable concentrations of these cations are present in rainwater, as shown in Table 4.7, and higher concentrations are found in terrestrial waters.

The temperature of natural waters exerts a large influence on their compositions. As shown in Table 4.7, hydrothermal water (natural waters collected at 220°C) can exhibit both larger concentrations and a much wider range of dissolved cations than ordinary ground water.

Water in granite formations, for example, may have a high silica content, so silicates entering water from borosilicate glass could produce a saturation effect (Hill and Grimwood 1978).

Silica is assumed present as H_4SiO_4 or higher polymeric species. Moreover, trace concentrations of other chemical species not shown in

TABLE 4.7. Representative Concentrations, ppm, of Cations and Silica in Natural Waters (adapted from Wedepohl 1967)

	Rain Water	Terrestrial Water	Hydrothermal Solution
Na	1.1	5.8	51,000
K	0.26	2.1	25,000
Ca	0.97	20	40,000
Mg	0.36	3.4	700
Si	0.83	8.1	>110
NH_4^+		–	500
Sr	–	–	700
Li	–	–	300
Ba	–	–	200
Rb	–	–	170
Cs	–	–	20
As	–	–	15
Fe	–	–	3200
Mn	–	–	2000
Al	–	–	300
Zn	–	–	970
Pb	–	–	100
Cu	–	–	10
Ag	–	–	1

Table 4.7 may be present. For instance, it has been proposed that an aluminosilicate complex is present in natural waters. Its equilibrium with an aluminosilicate surface film is hypothesized as being responsible for the long-term stability of many minerals in nature (Paces 1973).

Limited leach testing of solidified waste materials has been done with natural waters or with water in which some naturally occurring constituents have been simulated. Generally, when compared with results obtained by deionized water leaching, lower leach rates are obtained when the initial leachant contains cations or silica, but the differences are not large.

Workers at Harwell (Johnson and Marples 1979) have reported virtually no difference in the leaching of borosilicate glasses at ambient temperatures by distilled waters or sea water.

4.5.4 Anions and Organics in Leachants

Sulfate, chloride, and dissolved CO_2 as HCO_3^- or CO_3^- are ubiquitous in natural waters. Some representative concentrations in natural waters are given in Table 4.8. Complexing between these anions and many cationic constituents of nuclear waste may occur.

Strong chelate complexing of some of the cations is possible with humic and fulvic acids (Carroll 1970, p. 125). These organic compounds are present in at least the ppm concentration range in most terrestrial waters. Bacteria and fungi can also accelerate the attack on minerals in nature. The acceleration can be due to bacterial-induced oxidation of iron or uranium, for instance. Acceleration can occur also through bacterial production of carbonic, nitric, formic, or other acids (Winkler 1973, p. 155). The occurrence of organic compounds is not limited to surface waters. Shales, the most abundant sedimentary rocks, have an average carbon content of 0.5 to 0.6 wt%. Water in equilibrium with these rocks contains traces of organic material.

Only limited leach testing has been done in which the initial leachant contained organics. The results generally show that if there is a measurable

TABLE 4.8. Representative Concentrations, ppm, of Anions in Natural Waters (adapted from Wedepohl 1967)

	Rain-water	Terrestrial Water	Hydrothermal Solution
Cl^-	1.1	5.7	185,000
SO_4^{-2}	4.2	12	60
$HCO_3^- + CO_3^{-2}$	1.2	35	----
Br^-	----	----	150
F^-	----	----	18
I^-	----	----	22
BO_3^-	----	----	520

effect the leach rate increases and that the most marked effect results from the addition of organic chelating agents.

4.6 EFFECT OF RADIATION

Solidified radioactive wastes receive substantial radiation doses over long periods from radioactive decay of the incorporated radionuclides. Alpha, beta, and gamma radiations are associated with decay of actinides and fission products. Neutron radiation is also produced by (α, n) reactions when actinides are present and, to a smaller extent, by spontaneous fission. The fission fragments formed in fission reactions will likewise impart energy (i.e., contribute radiation dose) to the waste form.

A detailed discussion of radiation effects on nuclear waste forms is given in Section 6.0. Changes that can occur include transmutation effects, displacement events, oxidation-reduction reactions, and stored energy buildup.

Any of the radiation-induced changes discussed above may be related to changes in the leaching properties of nuclear waste forms. Leaching is a complex process that is expected to vary with changes in waste composition and physical properties. Furthermore, in the presence of locally intense radiation fields and the radiolysis products generated both in the solid waste form and in the contacting fluid, changes in the leaching mechanisms and rates may occur. For this reason, leaching experiments are most appropriately performed with radioactive specimens (if possible, with specimens fully loaded with the nuclear waste) that have received a range of radiation doses.

Irradiation with 3-MeV electrons to doses of 10^{11} rads has been reported to have little effect on the leach rate of borosilicate glass, but this treatment at temperatures above 550°C increases the leach rate of phosphate glass (Laude et al, 1976; Grover and Walmsley 1967, 1969), possibly because radiation increases devitrification effects at higher temperatures. The negligible effect of irradiation by energetic electrons to a dose of 1.2×10^{11} rads on the leach rate of glasses was also reported by workers in France (Jacquet-Francillon et al. 1978); a second leaching process carried out after 10 yr of storage indicated no change in the leaching rates of blocks containing

1000 Ci/ℓ of glass. Mendel (1977) has reported the absence of an irradiation effect on the leaching of borosilicate glasses after they received beta-gamma doses of 1 to 4.6 x 10^{11} rads. Gamma irradiations to a total dose of 10^{11} rads at ambient temperature (Johnson and Marples 1979) and at 350 to 789°C (Grover and Walmsley 1969) had no discernible effect on the durability of borosilicate glasses.

The leachability of strontium from concrete samples containing simulated Savannah River Plant (SRP) waste sludges was unaffected by gamma doses to 10^{10} rads, simulating a 100-yr dose from actual waste (Stone 1979).

McVay (1979) has studied the leaching behavior of a glass and a supercalcine in a gamma field of 2.4 x 10^6 R/hr for 310 hr (total dose 7.4 x 10^8 R). His results, reported as fractional leach rates in salt water and in deionized water, are shown in Table 4.9. In this study, the gamma irradiation during the leaching significantly affected the leach rates of most elements detected in the leachates.

Boult and coworkers (1979) prepared glass specimens doped with 5 wt% ^{238}Pu, which gave as many alpha decays/cm^3 in one year as the actual waste would receive in several hundred years. The specimens were leach-tested by a

TABLE 4.9. Fractional Release Rates Obtained During Gamma Irradiation of Glass and Supercalcine Samples (adapted from McVay 1979)

Element	7668-SW[a] γ-irradiation, $(cm^2 \bullet hr)^{-1}$	7668-DIW[b] γ-irradiation, $(cm^2 \bullet hr)^{-1}$	7668-DIW no irradiation, $(cm^2 \bullet hr)^{-1}$	SC-SW γ-irradiation, $(cm^2 \bullet hr)^{-1}$	SC-DIW γ-irradiation, $(cm^2 \bullet hr)^{-1}$	SC-DIW no irradiation, $(cm^2 \bullet hr)^{-1}$
Si	1.67×10^{-5}	2.27×10^{-5}	6.53×10^{-6}	1.03×10^{-5}	1.48×10^{-5}	3.24×10^{-6}
B	2.15×10^{-5}	2.80×10^{-5}	9.50×10^{-6}	--	--	--
Ca	3.39×10^{-5}	3.14×10^{-5}	4.41×10^{-6}	2.09×10^{-5}	1.38×10^{-5}	4.10×10^{-7}
Sr	1.87×10^{-5}	2.15×10^{-5}	4.89×10^{-6}	2.04×10^{-5}	2.15×10^{-5}	1.97×10^{-6}
Ba	9.98×10^{-6}	1.38×10^{-5}	1.16×10^{-6}	1.50×10^{-5}	1.54×10^{-5}	3.05×10^{-6}
Na	--	6.64×10^{-5}	1.22×10^{-5}	--	2.26×10^{-3}	9.50×10^{-5}
Cs	1.53×10^{-5}	1.83×10^{-5}	1.27×10^{-5}	3.1×10^{-6}	7.15×10^{-6}	5.05×10^{-6}
Mo	1.76×10^{-5}	2.58×20^{-5}	2.67×10^{-6}	2.23×10^{-5}	3.51×10^{-5}	5.33×10^{-6}
Ni	1.91×10^{-5}	2.53×10^{-5}	--	2.85×10^{-5}	2.93×10^{-5}	--
wt loss	$\frac{8.45 \times 10^{-5}\ g}{cm^2 \bullet d}$	$\frac{1.23 \times 10^{-4}\ g}{cm^2 \bullet d}$	$\frac{5.89 \times 10^{-5}\ g}{cm^2 \bullet d}$	$\frac{9.37 \times 10^{-6}\ g}{cm^2 \bullet d}$	$\frac{3.74 \times 10^{-5}\ g}{cm^2 \bullet d}$	

(a) Saltwater solution (700 ppm Na)
(b) Deionized water

Soxhlet technique at the intervals shown in Table 4.10. Although the specimens were not leach-tested immediately after being prepared, the leach rates obtained after one year's storage at 50 and 170°C were about as expected for specimens of this composition and were the same as those of $^{239}PuO_2$-containing control specimens. Leach rates increased about 50% following storage for a second year, but no apparent change occurred in the third year's storage. A specimen of the glass was also irradiated in a Van de Graaff accelerator to simulate 100 yr of storage. The increased leach rates observed with the electron-irradiated specimens may have been due simply to the annealing of the specimens, which resulted from the heating effect of the beam.

The effect of alpha radiation on the leaching of actinide elements from SRP waste glass has been examined by Bibler and Kelley (1978). Borosilicate glasses doped with ^{244}Cm and ^{238}Pu were leach-tested soon after fabrication and about 9 months later, as shown in Table 4.11. The radiation exposure appeared to have no effect on the leachability of these specimens. More than 10^6 years of storage would be necessary for the actual waste glass to accumulate the doses received by these specimens. The values in Table 4.11 also agree with those determined for the release of alpha radioactivity from test samples of glass containing actual SRP waste (Kelley 1975).

Radiation-induced changes in potential leaching fluids and in surrounding geomedia can also significantly affect release rates and the migration of radionuclides from waste forms in a repository. Jenks (1980) has reviewed

TABLE 4.10. ^{238}Pu-Doped Glasses Leach-Tested by Soxhlet Technique (adapted from Boult 1979)

Holding Temperature, °C		Total Dose Over 3 Yr, Disintegrations/g	Leach Rates, g/cm^2·d at 100°C, After		
First Year	Subsequent Years		1 Yr	2 Yr	3 Yr
50	20	2.7×10^{18}	1.6×10^{-3} 2.4×10^{-3}	2.3×10^{-3}	2.3×10^{-3}
170	20	2.7×10^{18}	1.5×10^{-3} 2.2×10^{-3}	2.3×10^{-3}	2.6×10^{-3}

TABLE 4.11. Leachability of ^{244}Cm and ^{238}Pu from Borosilicate Glasses Containing Simulated SRP Radioactive Waste[a] (adapted from Bibler and Kelley 1978)

Age of Glass, days[b]	Leachability, g/cm^2•d		Fraction Leached	
	^{244}Cm Glass	^{238}Pu Glass	^{244}Cm Glass	^{238}Pu Glass
6	0.16×10^{-8}	2.7×10^{-8}	0.14×10^{-8}	3.2×10^{-8}
274	0.34×10^{-8}	6.2×10^{-8}	0.29×10^{-8}	7.3×10^{-8}
275	0.98×10^{-8}	5.2×10^{-8}	0.84×10^{-8}	6.1×10^{-8}
276	0.70×10^{-8}	4.6×10^{-8}	0.60×10^{-8}	5.4×10^{-8}
277	0.56×10^{-8}	1.6×10^{-8}	0.48×10^{-8}	1.9×10^{-8}
278	0.21×10^{-8}	--	0.18×10^{-8}	--

(a) Waste was 50 mol% each of $Fe(OH)_3$ and MnO_2.

(b) Samples were leached in 150 ml of distilled water at ambient temperature for 24 hr. Fresh water was added daily.

information on the radiation chemistry effects in brines and salt deposits and has discussed the needs for additional experimental data.

4.7 EXTRAPOLATION OF LEACHING BEHAVIOR

Mathematical models are being used to evaluate the long-term safety of geologic disposal of nuclear waste. The safety analyses, or risk assessments, use a sequence of mathematical models (shown in Figure 4.14) to represent the pathway that radionuclides would have to travel from a repository through the intervening geological formations into contact with man. The radionuclide source term initiates the sequence. The source term is defined by the leach

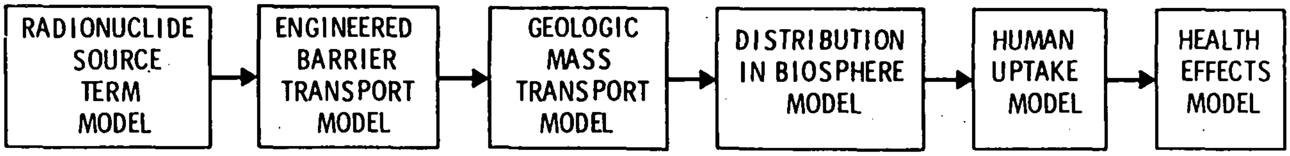

FIGURE 4.14. Mathematical Models Used in Safety Analysis of Geologic Disposal of Radioactive Waste

rate, or in some cases it may be defined by solubility and equilibrium considerations. This document deals only with the first model, which is important because it defines the quantity of radionuclides that feeds into the subsequent models.

4.7.1 Extrapolation Techniques Used in Risk Assessments

In the geologic-repository risk assessments that have been made, a constant fractional release rate from the waste form has usually been assumed (Koplik et al. 1979, Table 4.1-1). Use of a constant fractional release rate implies that a constant leach rate can be expected if water contacts the waste form in the repository. This is assumed because insufficient data exist to allow more sophisticated modeling. In most laboratory tests, however, the leach rates are not constant; they decrease with time, but they do appear to tend toward a constant rate as the duration of the experiment is extended.

4.7.2 Mechanisms Controlling Long-Term Leaching

The bulk leaching of waste solids, when they are contacted by aqueous fluids, will vary according to conditions of composition of fluid and solid, temperature, surface condition, surface-area to solution-volume ratio, geometric factors such as surface-to-volume ratio for the solid, and other factors. In general, leaching will follow a $t^{1/2}$ dependence, where t is equal to time, if the rate-determining steps involve simple diffusion; leaching will follow a t^1 dependence if the rate-determining steps involve simple corrosion. Thus, for the leaching of component "i" for which a $t^{1/2}$ dependence is observed, the fractional release of "i" at time t is given by

$$F_i(t) = at^{1/2} \tag{5}$$

where a is a constant. In the case of simple diffusion from a semi-infinite solid, a rigorous solution (Godbee and Joy 1974) is

$$F_i(t) = 2(S/V)(Dt/\pi)^{1/2} \tag{6}$$

where

S = surface area
V = volume of the solid sample
D = effective diffusivity of species "i" within the glassy solid
t = time of leaching experiment.

On the other hand, if corrosion is rate-determining, the relationship becomes

$$F_i(t) = bt \tag{7}$$

where b is a constant.

The generalized expression, showing the simultaneous dependency on diffusion and corrosion, which normally applies to glassy solids, is the following:

$$F_i(t) = at^{1/2} + bt. \tag{8}$$

In terms of the observed fractional release rate, the following expression applies:

$$R_i(t) = at^{-1/2} + b. \tag{9}$$

More complicated rate expressions apply for finite solids and for leaching in the later stages (e.g., $\geq$75% release); however, the simple expressions given here are useful for approximating the leaching process.

The release of ions from a solid to a liquid is controlled by mechanisms involving both the solid and the liquid (plus any film layers that may be present). The diffusion-controlled kinetics are affected by the rate at which the liquid moves past the solid as well as the concentration of ions in the liquid. In a stagnant or finite-volume leachant, a buildup of corrosion products can alter the observed rate, due to accumulation either in the leachant itself or in a surface film. Thus, the observed release rates depend upon such experimental leaching conditions as flow rate, pH, and liquid-to-solid ratio. Consequently, it is important to have standardized leaching conditions when comparing results of different laboratories and for different solid waste forms.

Uncertainties in the interpretation of leach data have forced mathematical modelers to make conservative assumptions. They have generally selected a single leach-rate value obtained from high flow rate, short-term tests. Thus the effects of the low flow rates that will generally predominate around the waste form are not incorporated.

The mathematical expressions used to model the leaching process have been either developed from first principles of mass transfer or derived empirically. For example, Godbee and Joy (1974) reported that a rigorously developed model, taking into account diffusion and matrix dissolution, agreed well with experimental data. Griffing (1974) showed that a somewhat different model could accurately describe the release of cesium from pollucite. Both authors noted that their models were applicable to specific mechanisms only and that other, often more complicated, models were sometimes necessary to describe the leaching process.

Empirical models are frequently used, especially when the leaching mechanism is unknown or the analytic solutions to the mass-transport equation are too complex for easy application. Ewest (1978) used an empirical approach for describing leaching processes in his "source-term model." Based on releases of sodium from a glass, the equation best fitting the data indicated that the leach rate depended on time to the two-thirds power rather than the one or one-half power. Lanza et al. (1980) fitted weight-loss data for a waste glass to a relationship similar to that of Equation (8). Although the model did fit the data well during the initial part of the test, the fit was much poorer after longer times.

Thus the mathematical agreement (precision) with experimental results that may be obtained with an empirical model may well be limited by the number and type of terms used. Furthermore, it is applicable only over the time range for which data are available. Extrapolations beyond the studied range of the leaching test must still be regarded as tenuous.

Much can be learned about anticipated long-term behavior by examination of natural systems. The long-term conditions encountered by natural systems during their entire history cannot be known exactly, but good estimates can be made. Thus natural systems can serve as long-term "proof tests" if correlations between waste forms and natural systems can be made. Short-term correlations have been made (Table 4.12 and Figure 4.15) and show that waste forms, such as glass, have chemical durabilities equal to or better than many natural materials, at least under the specific conditions of the tests. The problem remaining is to develop a good scientific basis for extrapolating the short-term correlations. One technique is to produce waste forms that resemble

TABLE 4.12. Comparison of the Chemical Durability (Soxhlet Test) of Waste Glass and Common Minerals (adapted from Ross 1975)

Minerals	Wt% Leached
Quartz crystals	0.41
Milky quartz	0.50
Dolomite	0.55
HLW glass	0.70
Garnet	0.73
Corundum	0.77
Orthoclase	0.90
Granite	1.10
Quartzite	1.20
Felsite	2.10
HLW glass (devitrified)	2.50
Marble (dolomite)	2.90
Calcite	5.80
Basalt	6.10

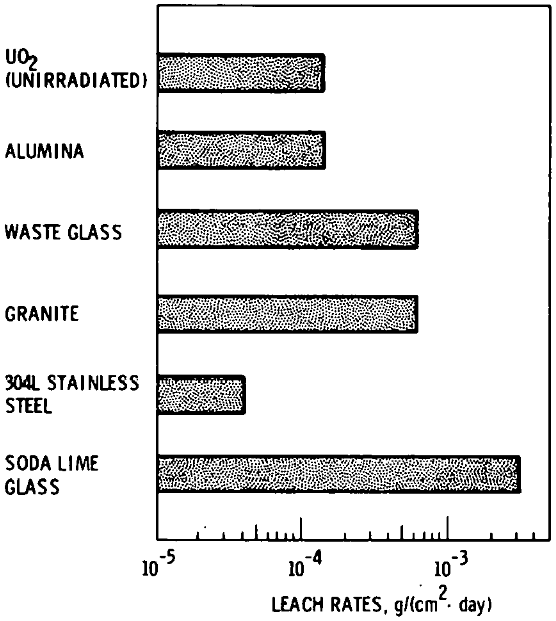

FIGURE 4.15. Leach Rates in 250°C Salt Brine, Based on Weight Loss (adapted from Mendel et al. 1980)

natural materials of demonstrated durability as closely as possible. That is a goal of much of the recent waste-form development. But improved techniques for extrapolating leach data are also needed.

Clearly, leach rates such as shown in Table 4.12 do not prevail in nature even after a temperature correction is applied. If they did, the land masses would have dissolved away long ago. The mere fact of persistence of the natural materials demonstrates that the short-term leach rates measured in the laboratory do not apply to long-term conditions. There are rate-inhibiting processes in the natural surroundings that protect natural materials and that may also slow the leaching of waste forms.

4.8 SPECIAL CONSIDERATIONS IN TEST EQUIPMENT AND OPERATION

Previous sections have discussed the effects of parameters such as temperature, solution composition, and radiation on the chemical durability of waste forms. These variables are important to consider when designing and selecting a waste form since they relate to conditions within a repository.

This section shows that the experimental methodology itself--analytical methods, sample preparation, and test equipment--can affect the apparent durability of a waste form.

Precise descriptions of the leaching conditions and the experimental precision of the results are frequently omitted from the literature. Experimental studies often involve small specimens and, for leach-resistant solid forms, only trace quantities are leached out of the solid during the experiment. Thus analysis of the leachates requires very sensitive techniques.

4.8.1 Analytical Techniques

Leach rates are typically calculated from weight-loss measurements or from solution analyses. Until recently weight loss was perhaps the most frequently used method to determine durability; however, it also provided the least information about the leaching process. Though simple and rapid, weight-loss measurements yield little information about the release of individual elements. Cement samples absorb water during leaching and, therefore, show weight gains rather than weight losses. Nevertheless, for glasses leached in deionized water, weight loss is related to the releases of some of the more mobile species. Figure 4.16, taken from Westsik and Harvey (1981), shows that actual weight losses were within a factor of three of the mass losses normalized to the behavior of sodium, boron, molybdenum, silicon, cesium, and phosphorus.

If weight losses are to be measured, the specimens must be prepared and handled carefully. Surface cleaning is important; many procedures call for ultrasonic cleaning in organic solvents before making weight measurements. One particular concern is the formation of surface films during leaching. Some workers prefer to remove this film prior to final weighing, while others leave the film intact. It is generally recognized that drying will cause cracking of the gelatinous surface films and that, therefore, a sample should not be reused after drying.

Solution analyses are required for obtaining detailed information about the leaching processes. But experimental problems arise in measuring the low concentrations of species released into solution. Although modern chemical

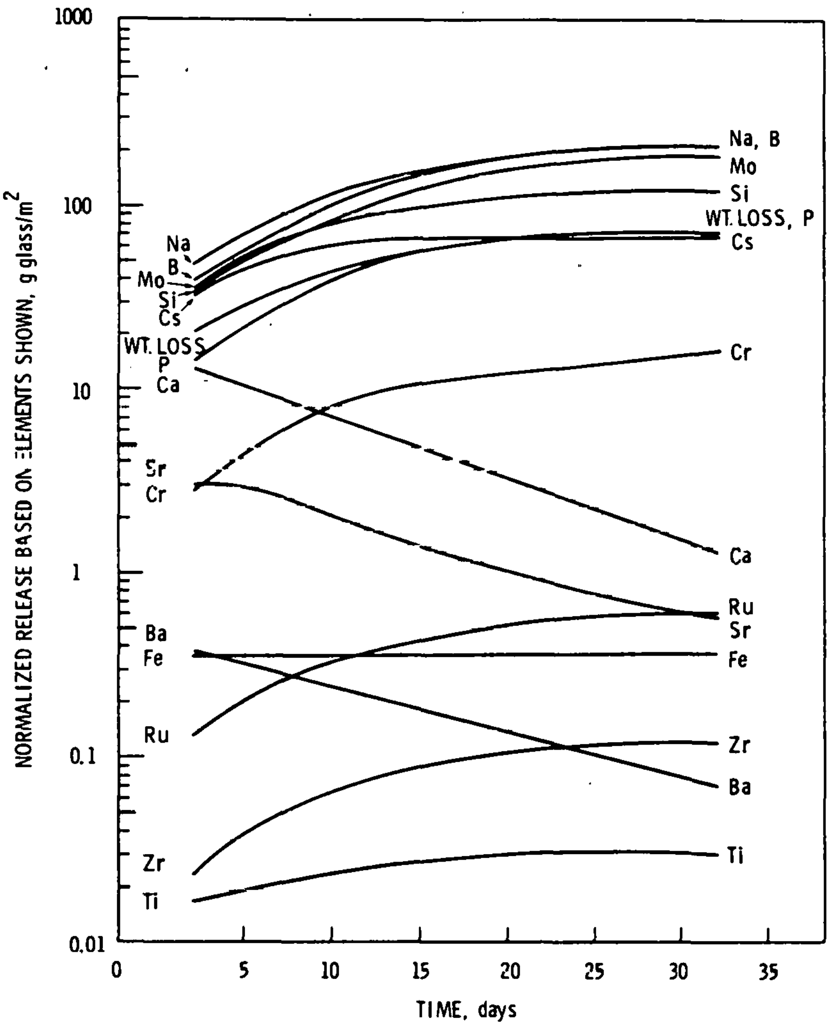

FIGURE 4.16. Releases of Nonradioactive Species from PNL 76-68 Glass into 150°C Deionized Water

and radiochemical techniques have lowered detection limits for many elements to the parts-per-billion level, even some of the most modern experimental procedures may need to be modified.

Analytical precision can be improved by increasing the amount of material in solution. Since leaching is basically a surface phenomenon, increasing the surface area of the samples will result in higher solution concentrations for a given exposure time. Where pH influences the leaching mechanism, changing the ratio of solution volume to sample surface area may change the apparent leach rates obtained for a given waste form (Hench 1977).

Other methods to increase solution concentrations for a given time of exposure include leaching at elevated temperatures or evaporating the leachate prior to analysis. Kelley and Wallace (1976) developed a unique method of concentrating the leached ions. The leachate from a flowing system was passed through an ion-exchange column before being recycled. The ions, concentrated in the ion-exchange resin, were later eluted from the resin column and analyzed.

The potential for solubility effects on sorption behavior should be considered in experimental design. Many workers acidify the leachate or add complexing agents to ensure that all leached species remain in solution. Materials that have deposited on the leachant container walls may be removed by rinsing with acids. Bradley et al. (1979) have found that a 5<u>M</u> HNO_3 - 0.05<u>M</u> HF solution effectively removes actinides that have "plated out" on leachant container walls. Other researchers simply count the leachant container with the leachate (Scheffler and Krause 1977).

Radioactive tracers can be used to follow the leaching of ions from a waste form and to improve the precision of measurements. Tracers have low detection limits and can label leached species in leachants that may already contain nonradioactive isotopes of those species. Individual radioisotopes may be used, or actual radioactive wastes may serve as a source of tracers.

To overcome some of the analytical limitations associated with leaching tests, Argonne National Laboratory has used neutron activation analysis in conjunction with leachability experiments (Steindler et al. 1978, 1979; Flynn et al. 1979). Radiotracer tags are generated in the waste form by neutron irradiation of the specimen prior to leaching. The amounts of induced radioactivities are determined; the solid matrices are leached; and the fractional amount of radioactivity removed from the solid is measured for each radionuclide. Unfortunately, the method is limited to only certain elements. The leach rate of a radiotracer produced in situ may differ from that of an incorporated radionuclide. Furthermore, the radiation-induced changes in the irradiated samples (though expected to be small) have not been determined. However, this approach is useful for measuring the leach rates for durable waste forms. Neutron activation analysis has also been used by Idaho workers to obtain elemental leach rates of zirconia waste glass in distilled water (Plung 1979). In these experiments, ~10 mg glass samples and evaporated aliquots of leach solutions were irradiated and then analyzed.

4.8.2 Surface Preparation and Specimen Configuration

The geometry of the specimen and the surface condition are perhaps the largest source of variability in leach-rate measurements. Surface effects include residual stresses and elemental concentrations different from those of the bulk of the material. The first data points from a leach test are sometimes disregarded to avoid including the nonreproducible surface effects. Another option is to run the test long enough to make such effects insignificant.

Specimen surfaces may not initially contain a full complement of elements or phases when compared with the bulk material. For instance, volatility losses incurred by high-temperature waste forms may deplete the surfaces of some species. Canadian workers have shown that unleached glass specimens that had been polished by metallography were depleted in sodium to a depth of 60 nm (Bradley et al. 1979). Sanders and Hench (1973) have shown that surface roughness also can influence the apparent durability. They found that the amounts and the relative proportions of elements leached from a simple lithium-silicate glass depended on the roughness of the surface finish.

Powdered specimens are often used to increase the specimen surface area so that more ions are released to the leachate. While this makes chemical analysis easier, it also complicates interpretation of results. Increasing the surface area while keeping the solution volume constant may produce changes in the chemical properties of the solution, thereby influencing the leaching mechanism. Unless the powder is well dispersed or the system is agitated, mass transfer of leachate ions can be hindered. Figure 4.17 compares leach data for -42 + 60 mesh powder and monolithic samples of the same glass under nonagitated conditions (Ross et al. 1978). The observed difference of nearly two orders of magnitude is postulated to result partly from the fact that, in the loosely packed powder, the leached ions must diffuse through a maze of stagnant interstitial fluids to reach the bulk of the solution. Because of

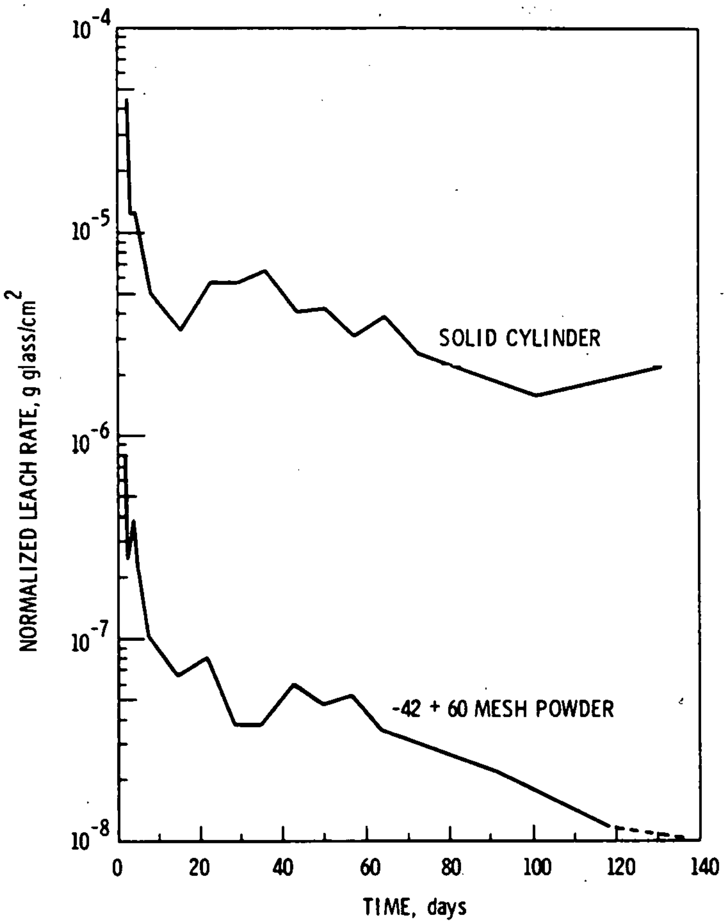

FIGURE 4.17. Normalized Leach Rates Based on Cesium from Solid and Powdered Samples of PNL 76-68 Glass

this effect, the powder appears to be much more durable than a monolithic solid of the same composition. This fact should be considered when cracked or composite waste forms with relatively large surface areas are leached. The surface effectively available for leaching may be significantly less in area than the actual physical surface area of extensively cracked, composite, or powdered waste forms.

Two techniques are used to determine the surface area of leach-test specimens. The geometric method involves calculations using physical dimensions. Alternatively, the surface area can be determined by the BET gas adsorption method (Brunauer et al. 1938). Since a rough or porous waste form can have a much larger BET than geometric surface area, using the BET value can make the waste form appear to be more durable than justified. Waste forms are commonly compared on the basis of their geometric surface areas; however, BET surface areas are still useful, especially in the study of leaching mechanisms.

4.8.3 Equipment

Design and construction of apparatus for leach testing requires selection of materials and instrumentation that do not affect the apparent durability of the waste forms being tested. Leachant containers must be made of materials that do not alter the chemistry of the leaching system. Plastics are most frequently used. The primary limitation of most plastics is in their poor tolerance of high temperature and radiation. Of the plastics, Teflon® exhibits good high-temperature tolerance and is also relatively inert. All plastics have some tendency to release trace quantities of contaminants to the leachant (Robertson 1972).

Glass containers should generally be avoided since glass itself is leachable. Metal containers are used at high temperatures, and metals are often used to support the waste-form specimen within the leachant container. Unless properly selected, the metal may react with the leachant, especially if salts are present. At higher temperatures, metals may act as oxygen fugacity buffers. For example, Ni-Ni oxide is often used by geochemists to control fugacity in hydrothermal testing. Metals in the leaching apparatus may also undergo galvanic reaction with metallic waste forms, such as cermets, and multibarrier waste forms. An Oak Ridge National Laboratory cermet, which was leached in deionized water, exhibited some surface pitting due to galvanic reaction between the Ni-based waste form and a stainless-steel wire used to suspend the sample in the leachant (Aaron et al. 1979).

As discussed in Section 4.4, temperature plays an important role in the durability of a waste form. Temperature control is necessary if reproducible test results are to be obtained when leaching a waste form. A 2°C difference in temperature at about 25°C can cause a 12 to 25% change in the leach rates.

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4.8.4 Statistical Analysis of Leach Test Data

Table 4.13 shows the precision obtained in some leach studies. The observed variations are attributable to various factors, including 1) specimen preparation, 2) heterogeneity of waste forms, 3) sampling procedures and analytical methods, and 4) deviations from the test procedure.

The precision of leach tests can be improved through use of rigorous standard procedures. In developing standard procedures, experiments must be conducted to identify those parameters that can significantly affect the apparent durability of a waste form. These factors must then be stringently controlled in the final procedure (Mendel et al. 1980). Standard specimens with certified leach rates can then serve as a check to verify that the procedure is being followed.

4.9 CHEMICAL DURABILITY OF ALTERNATIVE WASTE FORMS

One meaningful comparison of the chemical durability of waste forms is based on the "steady-state" release rates that can be defined to occur under stated conditions (which will be repository-site-specific). These can be related directly to the NRC's repository release criterion, which for HLW is presently proposed to be 10^{-5}/yr of the radionuclide inventory present after 1000 years. The technology for making quantitative comparisons on a standardized "steady-state" release basis is not yet in place; to provide standardization of the technology that can define radioactive release from waste forms on a quantitative release is one of the purposes of the Materials Characterization Center.

TABLE 4.13. Typical Experimental Precision Observed in Leaching Tests

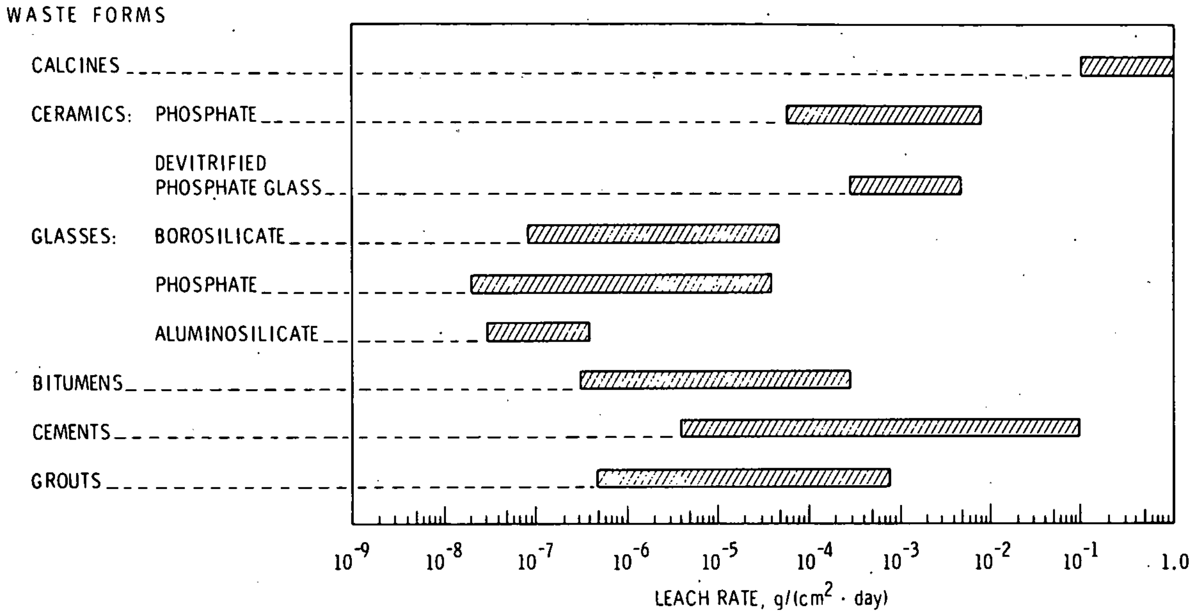
Waste Form	Precision	Reference
Concrete	<30%, not statistically different	Stone (1977)
Grout	Factor of 2	Moore et al. (1975)
NBS GLASS 710	Factor of 5 to 10	Kelley and Wallace (1976)
Fly ash	±50 to 75%	Gulledge and Webster (1979)

Actually, as can be inferred from Figure 4.18, which is an early attempt to compare waste forms using nonstandardized leach data, after 1000 years the differences in release rates among waste forms probably becomes relatively indistinct. This is because the actinides, which are the predominant radionuclides remaining after 1000 years, tend to have more or less the same leach rate from various waste forms, probably because of solubility limitations. Furthermore, depending on the assumptions made regarding surface area, a leach rate in the range of 10^{-7} to 10^{-8} g/cm^2-day corresponds to a release fraction of 10^{-5}/yr. Thus, although far more data are needed on the actinides, and on the behavior of long-lived nonactinide radionuclides such as ^{99}Tc, many different waste forms can probably achieve the proposed 10^{-5}/yr fractional release criterion after 1000 years.

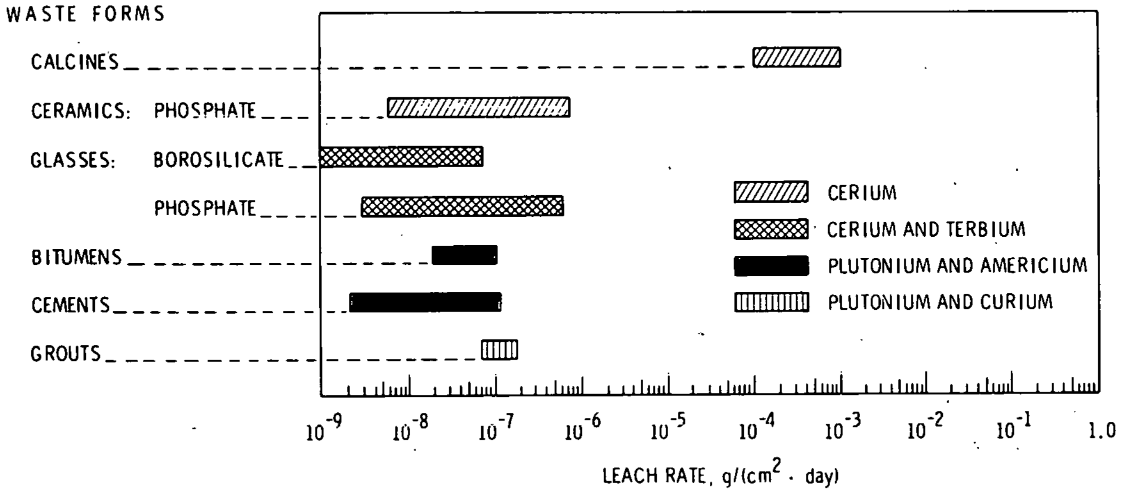
The reasoning outlined above has led waste form developers to emphasize behavior during the 0 to 1000 year period in the repository, when distinctions between waste forms are greatest. During this period the waste form is the innermost component of the waste package, from which the NRC draft criterion requires reasonable assurance that there be no release of radioactivity for 1000 years. In the event that water does penetrate through the multiple barriers of the waste package during this period and contact the waste form, the function of the waste form is to limit the amount of dissolved waste material to that which will not "overload" the adsorption or retention capacity of the other components of the waste package in <1000 years. It is not yet possible to make waste package-specific tests; the waste package systems are still under development, and will probably differ for different repositories. Thus testing of alternative waste forms has tended to be on a comparison basis, using deionized water or simple generic leachant fluids, but at temperatures representative of 0 to 1000 years.

4.9.1 Glasses

Modifications appear feasible in borosilicate waste glass compositions that yield an improvement of about a factor of ten over most of the borosilicate waste glass chemical durability data cited in the previous sections



a. Leach Rates of Alkali and Alkaline-Earth Elements from Various Waste Products



b. Leach Rates of Rare Earths and Actinide Elements from Various Waste Products

FIGURE 4.18. Comparison of Leach Rates (adapted from ORNL-5050)

(Chick and Backwalter 1980). The modifications involve lowering the fission-product loading, as in defense HLW glasses, or increasing the silica concentration and hence the melting point. (See Figure 4.19 and Table 4.14.)

High melting points (>1200°C) are generally considered undesirable for waste glasses because of the increased volatility of radionuclides during processing and the decreased lifetime of the processing equipment due to accelerated corrosion. Therefore, processing techniques that utilize reactive mixing (with alkoxides) or porous high-silica matrices are being investigated for application to Savannah River HLW. These techniques produce high-melting, more durable waste glasses at temperatures of 1200°C, or below. Soxhlet leach tests conducted at 100°C for 24 days typically showed release rates of $\sim 10^{-9}$ total g/cm^2-day for alkoxide-derived glasses of the approximate compositions

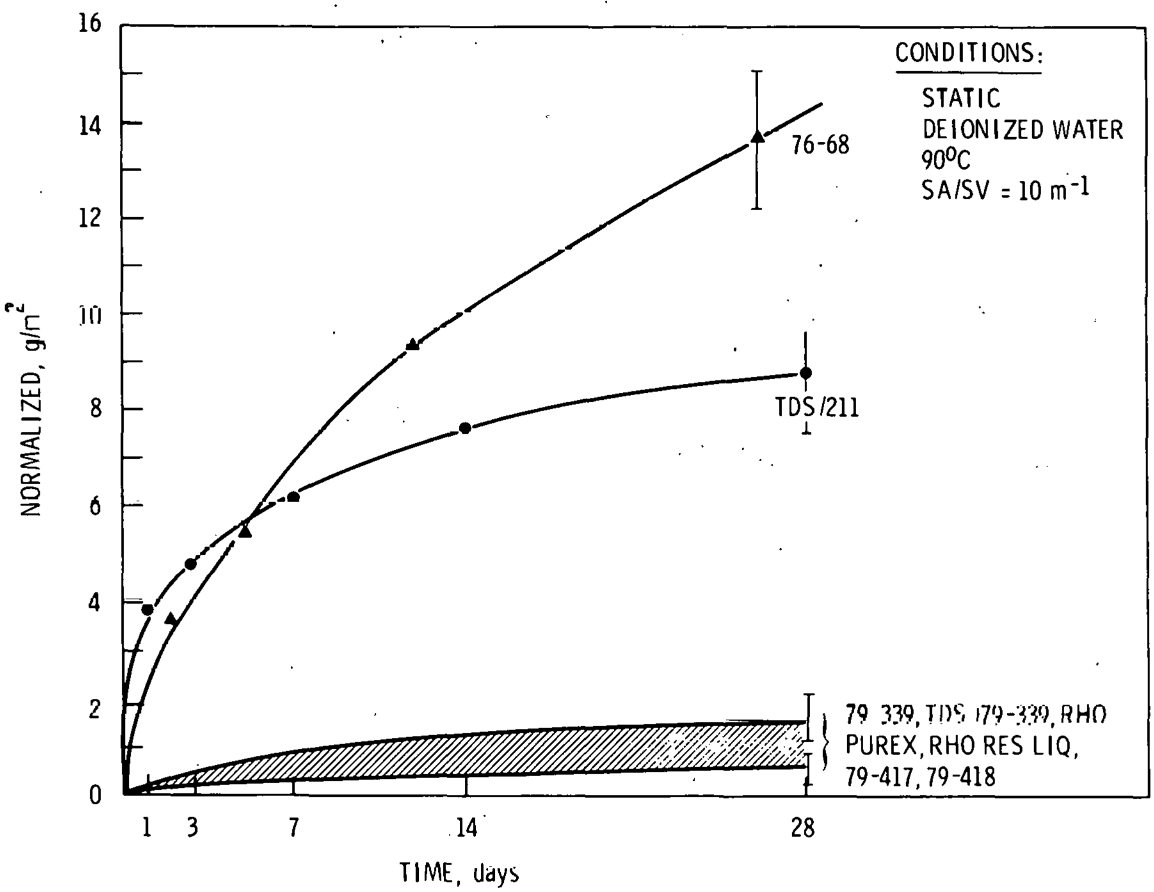


FIGURE 4.19. Cumulative Silicon Released Versus Time at 90°C (adapted from Chick and Buckwalter 1980)

TABLE 4.14. Compositions of Test Glasses, mole%, Melting Temperatures, and 28-Day Silicon Releases (from Chick and Buckwalter 1980)

Oxide	High-Durability Base Glass 79-339	Defense Waste Glasses TDS+ 79-339	TDS/211 Reference	RHO Purex	RHO Res. Liq.	Commercial Waste Glasses 76-68[a] Reference	77-260 Reference	79-417	79-418
SiO_2	66.0	63.2	49.8	57.4	67.0	51.7	49.8	61.4	63.7
B_2O_3	10.5	10.0	7.7	9.8	9.2	10.6	10.7	10.5	10.5
Al_2O_3	4.1	3.9	2.1	3.5	4.2	--	1.6	3.5	4.1
Na_2O	10.8	10.1	16.3	10.7	10.9	15.7	15.0	10.6	11.4
Li_2O	--	--	7.1	10.9	4.3	--	--	--	--
Cs_2O	--	0.2	0.2	--	0.1	0.3	0.2	0.5	0.2
K_2O	--	--	--	--	--	--	1.8	0.1	--
CaO	1.2	1.2	6.0	1.0	--	2.8	1.5	0.4	0.1
SrO	--	0.3	0.3	0.4	--	0.3	0.2	0.6	0.2
NiO	--	1.7	1.6	--	--	0.2	--	0.1	--
MnO_2	1.1	3.1	2.9	0.9	--	--	0.1	0.1	--
TiO_2	--	--	--	--	4.2	2.9	6.3	--	--
Fe_2O_3	6.3	6.3	6.0	5.4	--	4.8	0.6	0.7	6.5
Cr_2O_3	--	--	--	--	0.1	0.2	--	0.2	0.1
ZnO	--	--	--	--	--	4.8	--	0.2	0.1
CuO	--	--	--	--	--	--	3.2	--	--
Gd_2O_3	--	--	--	--	--	--	2.4	--	--
ZrO_2	--	--	--	--	--	1.1	1.1	2.2	0.6
MoO_3	--	--	--	--	--	1.0	0.9	2.2	0.6
Minor[a] Components	--	--	--	--	--	3.6	4.6	6.7	1.9
Melt temperature,[b] °C	1350	1350	1050	1100	1200	1150	1150	1350	1350
Silicon released[c]	0.5	0.7	8.8	1.1	0.6	14.0	NA	1.1	1.6
Resulting pH[d]	4.2	4.2	7.7	4.8	3.8	8.1	NA	4.7	6.1

(a) Minor components each less than 1 mole%.
(b) Temperature at which leach test samples were melted.
(c) Silicon released (normalized g/m^2) after 28 days, 90°C in deionized water leachant at SA/SV = 10 m^{-1}.
(d) Resulting pH measured in leachate after 28 days at 90°C at SA/SV = 10 m^{-1}. Initial pH of deionized water leachant was 5.7.

shown in Table 4.15 (Cornman 1981). In static tests performed at 70°C for 3 to 6 days some of the best porous high-silica glasses (composition not reported) exhibited leach rates of 2 x 10^{-8} g/cm^2-day versus 7 x 10^6 g/cm^2-day for a conventional borosilicate waste glass (Cornman 1981).

4.9.2 High-Fired Crystalline Materials

Examples of high-fired crystalline materials under development currently are SYNROC and high-alumina ceramics.

SYNROC is a crystalline assemblage in which the waste is incorporated in synthetic minerals, mainly titanates, and consolidated by some form of hot-pressing. The chemical durability of SYNROC is usually found to be somewhat better than borosilicate glass (< factor of 10) in short-term leach tests at 25 to 50°C. At higher temperatures the difference in leach rate becomes more marked (see Figure 4.20). When tests are extended in time, the differences also become larger, that is, the leach rate of SYNROC decreases with time more rapidly than does the leach rate of borosilicate glass (see Figure 4.21).

The high-alumina ceramics take advantage of the fact that aluminum is already a major constituent of Savannah River HLW; thus high waste loadings are possible in the final product. It is a dense ceramic, containing a

TABLE 4.15. Composition of Alkoxide-Derived Glasses (adapted from Cornman 1981), wt%

Constituent	Low-Alumina Formulation	Medium-Alumina Formulation
SiO_2	46.8	39.8
Al_2O_3	6.4	13.4
B_2O_3	10.5	10.5
Na_2O	10.6	10.6
Fe_2O_3	14.4	14.4
MnO_2	4.1	4.1
U_3O_8	1.3	1.3
CaO	1.1	1.1
NiO	1.8	1.8
Ion-Siv	3.0	3.0

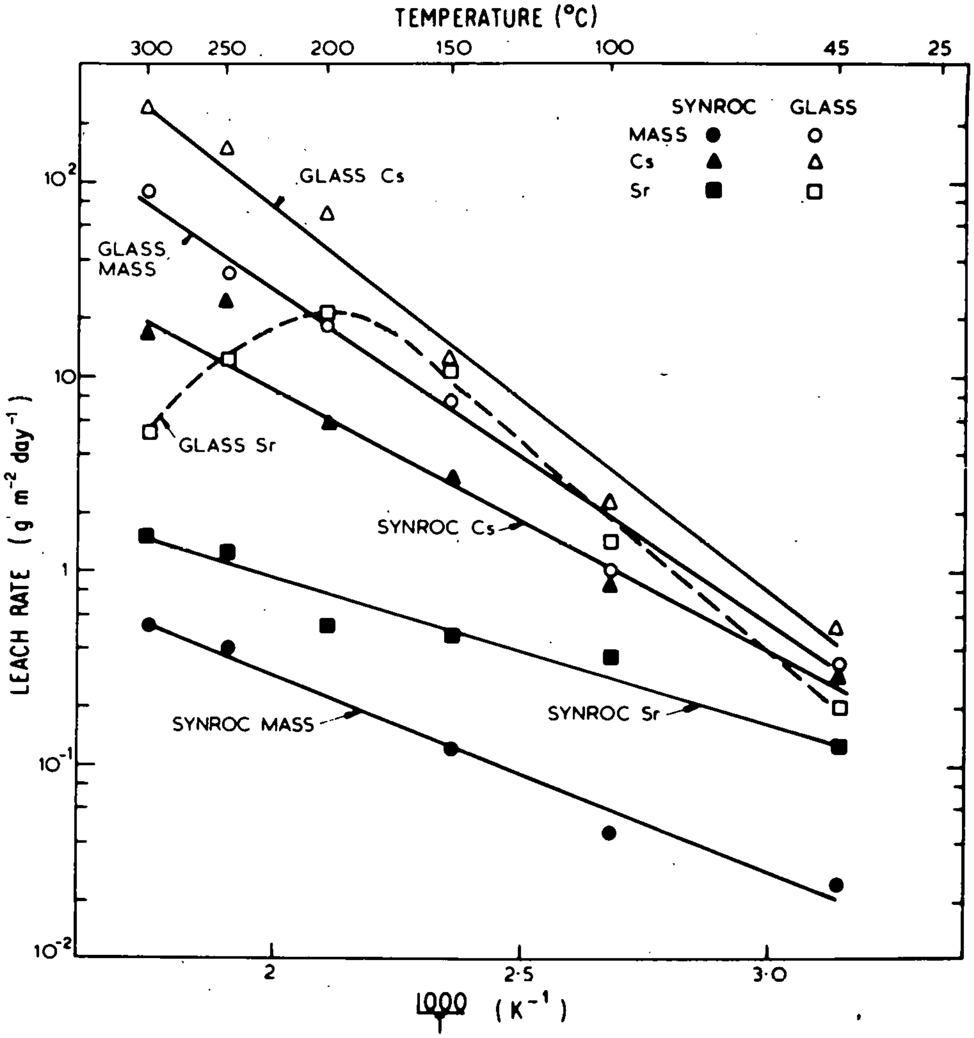


FIGURE 4.20. Effect of Temperature on Initial Leach Rate of SYNROC and Borosilicate Glass (PNL 73-1) Containing 10 wt% Simulated Radwaste (adapted from Reeve et al. 1981). Leachant: deionized water; leaching time: 1 day; leachant volume/sample surface area = 0.1 m.

mixture of crystalline phases, present with a small (<1 μm), uniform grain size, containing no continuous intergranular amorphous phases that is formed by hot isostatic processing at ~50,000 psi below 1200°C. Harker et al. (1980) reported that leach rates based on sodium and cesium behavior were about 1 x 10^{-5} g/cm^2-day for the high-alumina ceramics versus 10^{-4} to 10^{-3} g/cm^2-day for 76-68 and SRL borosilicate glass. The comparison was based on static tests in DI water performed at 90°C.

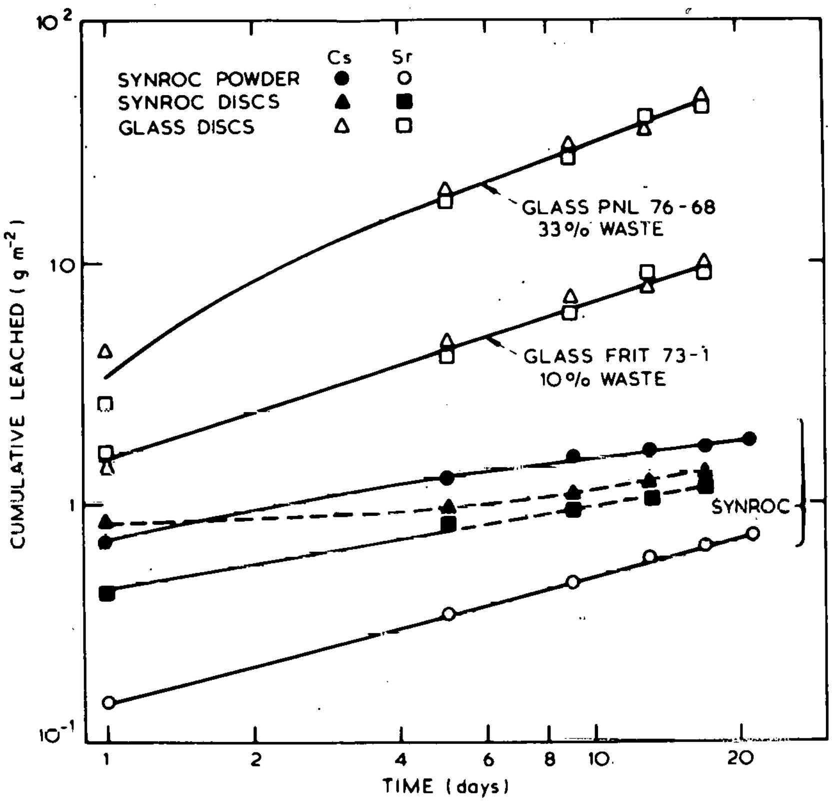


FIGURE 4.21. Cumulative Quantities of Cesium and Strontium Leached from SYNROC and Borosilicate Glasses (adapted from Reeve et al. 1981). Leachant: deionized water replaced daily; temperature: 100°C; for discs: leachant volume/area = 0.1 m; for 100-150 mesh powders: leachant volume/geometric surface area = 0.0017 m.

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5.0 VAPORIZATION

W. J. Gray

Vaporization data on nuclear waste forms are required for determining the risk from such unlikely events as shipping or storage accidents involving fire. In certain unlikely scenarios, loss of coolant during storage can also result in temperatures high enough for vaporization to occur (ARH-2799).

Because risks from vaporization are perceived to be relatively small even when compared with the very small risks associated with leaching, vaporization has received little attention. Very few vaporization studies have been done on either actual or simulated radioactive waste (Wilding and Rhodes 1966; Albrethson and Schwendiman 1967; Walmsley, Sammons, and Grover 1969; Lynch et al. 1975; Kupfer and Schulz 1977; Wilds 1978a; and Gray 1980), and a few other studies supporting radioactive waste programs have been performed using relatively simple glasses or ceramics (Mukherji 1971, Terai and Kosaka 1976, and Nikiforov et al. 1979). The methods used to generate the data in these studies were simple weight-loss techniques similar to transpiration experiments except that nonequilibrium conditions generally prevailed. Losses of specific constituents were determined by chemical analyses of the vapors or by analyses of the samples before and after vaporization. The latter approach makes it difficult or impossible to detect minor losses. In those studies where the vapors were analyzed, it was not always clear that all vapors were successfully collected and analyzed. As a result of these difficulties, accurate quantitative comparisons of data between different laboratories are almost impossible. However, test results from different waste forms within a given laboratory can be compared, and certain qualitative similarities between results from the different laboratories are apparent.

Data obtained by Gray (1980, 1976) were chosen for presentation in this chapter because they represent the only known work on simulated waste forms where all the vapor components, both fission products and other elements, were analyzed. His work also involved several different simulated waste forms, which permits comparisons between them. The reader is cautioned, however, that vapor compositions were estimated from only a partial collection of the vapors (using a "cold finger") and that very recent work by Gray shows this introduces some errors (e.g., cesium losses appear to be overestimated by a factor of about two.)

5.1 WASTE COMPOSITIONS

Compositions of the materials are listed in Tables 5.1 and 5.2. Nonradioactive isotopes were used throughout, and rare earths were substituted for actinides in all cases to facilitate handling. The first four materials listed in Table 5.1 are glasses; the last two are so-called supercalcines that contain chemicals added to produce appropriate crystalline phases to tie up the most hazardous fission products (McCarthy 1977).

5.2 VAPORIZATION DATA

Vaporization depends strongly on time, temperature, and composition. It also depends on the atmosphere, but studies of waste forms have employed an air atmosphere as the expected condition. Some studies have varied the air's moisture content. Vaporization also depends somewhat on the viscosity of glass melts. Each of these parameters is discussed separately, although there must necessarily be some overlap; and there is also a separate discussion on composition of the vaporized material.

5.2.1 Time Dependence

Results shown in Figure 5.1 typify all the glasses studied in that the weight losses are roughly proportional to t^n where t is time and n varies between 1/2 at high temperature and 1 at lower temperatures. Similar behavior was also found by Terai and Kosaka (1976) for some of the glasses they studied. Dependence on $t^{1/2}$ is usually taken to imply that the vaporization rate is limited by the rate of diffusion of the vaporizing elements to a depleted surface region. Linear time dependence is taken to imply that a surface reaction is the rate-limiting step. However, different rate-limiting mechanisms at the different temperatures are inconsistent with the linear Arrhenius plots described in the following section. Thus, the question of whether or not there are different rate-limiting mechanisms at the different temperatures remains unresolved.

TABLE 5.1. Waste Form Compositions

	Nominal Concentration, wt%					
Constituent	77-260(a)	76-68(a)	72-68	76-183	SPC-2	SPC-4
B_2O_3	8.93	9.47	11.30	9.50	--	--
Na_2O	11.36	12.80	4.12	11.64	0.18	0.19
MgO	--	--	1.50	--	--	--
Al_2O_3	2.00	--	--	1.00	4.43	4.53
SiO_2	35.80	39.80	27.71	35.50	19.00	17.64
P_2O_5	2.54	0.51	0.44	3.36	4.16	4.26
K_2O	2.00	--	4.12	2.00	--	--
CaO	1.00	2.00	1.50	2.00	4.93	2.09
TiO_2	6.00	2.97	--	6.00	--	--
Cr_2O_3	0.02	0.44	0.23	0.19	0.54	0.55
MnO_2	0.11	--	--	--	--	--
Fe_2O_3	1.31	10.34	1.00	1.60	4.68	4.79
Co_2O_3	--	--	--	0.16	--	--
NiO	0.01	0.21	0.09	0.56	0.22	0.22
CuO	3.00	--	--	3.00	--	--
ZnO	--	4.97	21.64	--	--	--
Rb_2O	0.12	0.13	0.23	0.19	0.55	0.56
SrO	0.31	0.40	2.20	0.56	2.86	4.23
ZrO_2	1.62	1.88	3.28	2.62	7.66	7.84
MoO_3	2.14	2.42	4.29	3.38	8.02	8.21
RuO_2	0.93	1.13	1.97	1.57	0.47	0.48
Rh_2O_3	0.17	0.18	0.32	--	--	--
PdO	0.53	0.56	0.98	--	--	--
Ag_2O	0.02	0.03	0.06	0.05	--	0.14
CdO	0.03	0.04	0.06	0.05	0.15	0.15
TeO_2	0.24	0.28	0.48	0.39	--	--
Cs_2O	0.85	1.09	1.91	1.53	4.46	4.57
BaO	0.59	0.59	2.54	0.83	2.43	2.48
RE_2O_3	18.12	7.76	8.03	12.34	35.26(b)	37.07(b)
Total	99.75	100.00	100.00	100.02	100.00	100.00

(a) No chemical analyses of vapor composition were made for these wastes.
(b) See Table 5.2 for rare-earth composition of the supercalcines.

TABLE 5.2. Rare-Earth Composition of Supercalcines

Element	Nominal Concentration of Oxide, wt% SPC-2	Nominal Concentration of Oxide, wt% SPC-4
La	9.0	1.4
Ce	16.3	5.1
Pr	1.8	0.3
Nd	6.1	13.3
Sm	1.1	0.2
Gd	0.7	16.6
Others	0.2	0.2
Total	35.2	37.1

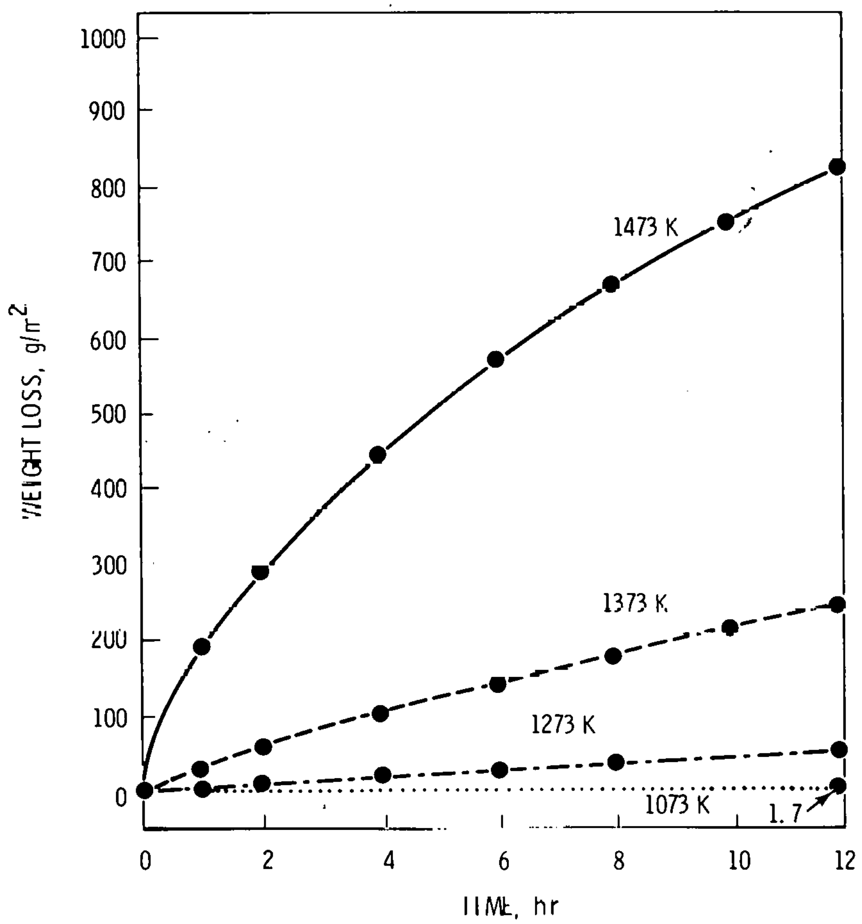

FIGURE 5.1. Weight Loss of 72-68 Glass in Dry Air

Time dependence of the vaporization for the non-glass materials was generally intermediate between t and $t^{1/2}$ (Gray 1980).

5.2.2 Temperature Dependence

Each of the glasses and supercalcines studied at PNL vaporizes with a single activation energy over the entire temperature range studied, as shown by the linear Arrhenius plots in Figure 5.2. Weight losses were reproducible only to about ±1 to 2 g/m^2; therefore, the low-temperature points are within experimental error of the lines drawn. The reasons for the anomalously low points for SPC-4 above 1200°C and for 72-68 glass at 1250°C are not relevant here and have been discussed previously (Gray 1980).

All the glasses vaporize with about the same temperature dependence, and a heat of vaporization of about 250 kJ/mol can be calculated from the slopes of the lines in Figure 5.2. Furthermore, the individual elements vaporize from the glasses with about the same temperature dependence; typical data are shown in Figure 5.3. This means that the composition of the vapor is nearly independent of temperature; only the vaporization rate changes.

The individual elements also vaporize from the supercalcine with temperature dependences that are about equal, as shown by Figure 5.4. The different slopes for the two different supercalcines are discussed in Section 5.2.4.

It is tempting to extrapolate the data in Figure 5.2 to lower temperatures to estimate long-term vaporization losses where such losses are too small to measure conveniently. Actual measurements by other workers, however, suggest this extrapolation may underestimate actual losses by a large margin. Walmsley, Sammons, and Grover (1969) reported cesium losses of a few hundredths of a percent after a few hundred hours at 400 to 500°C. Nikiforov et al. (1979) found a cesium loss of $\sim 5 \times 10^{-8}$ $g/cm^2 \cdot$ day at 400°C from borosilicate glass containing 2 wt% Cs_2O. These values can be compared with total weight losses of 10^{-10} to 10^{-7}% (10^{-12} to 10^{-9} g/cm^2) in 4 hr when the glass data in Figure 5.2 are extrapolated to 400 to 500°C. These differences between extrapolated and measured losses are several orders of magnitude, which are larger than one would expect even though the glasses in these separate studies are quite different.

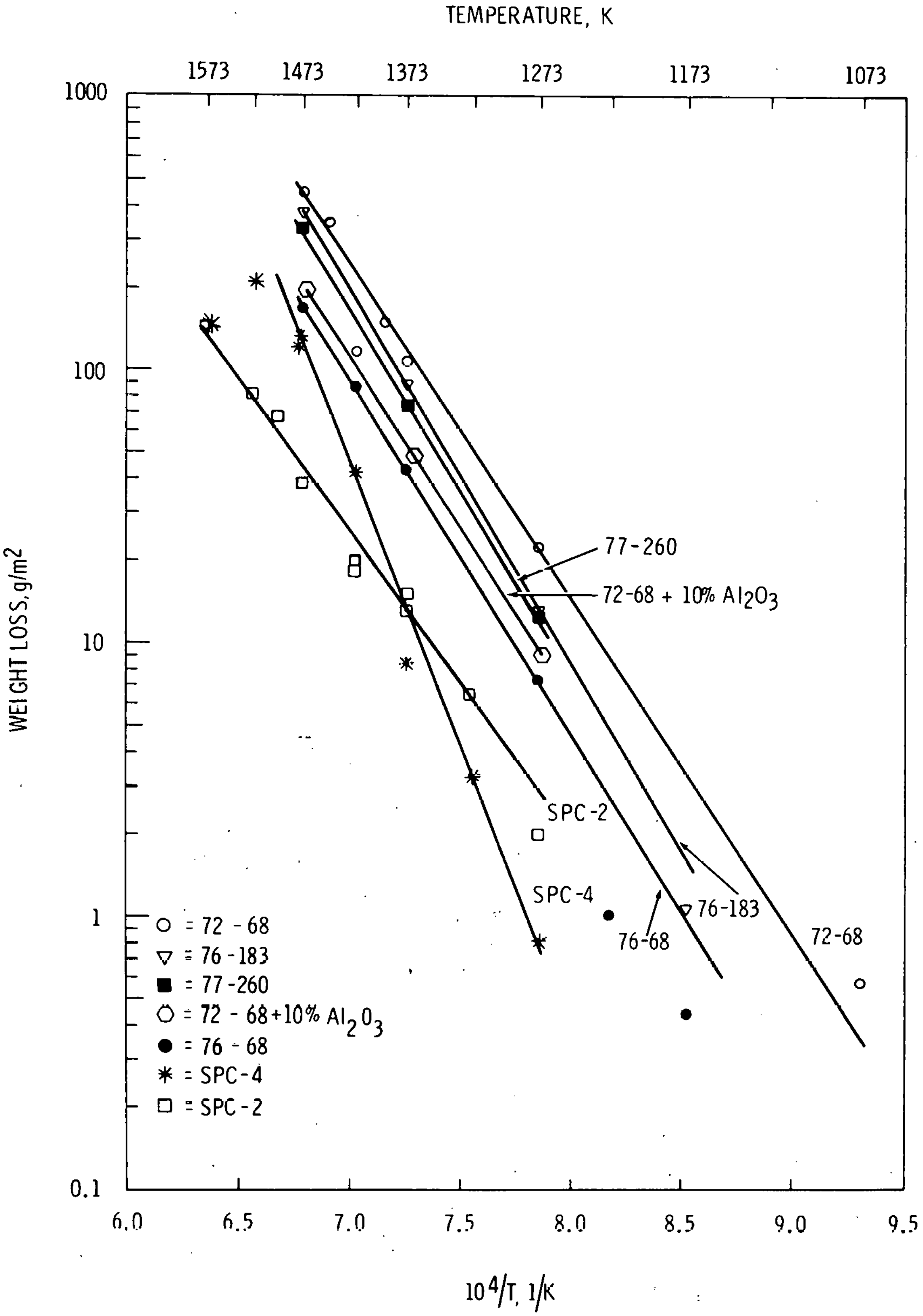

FIGURE 5.2. Weight Loss After 4 hr in Dry Air

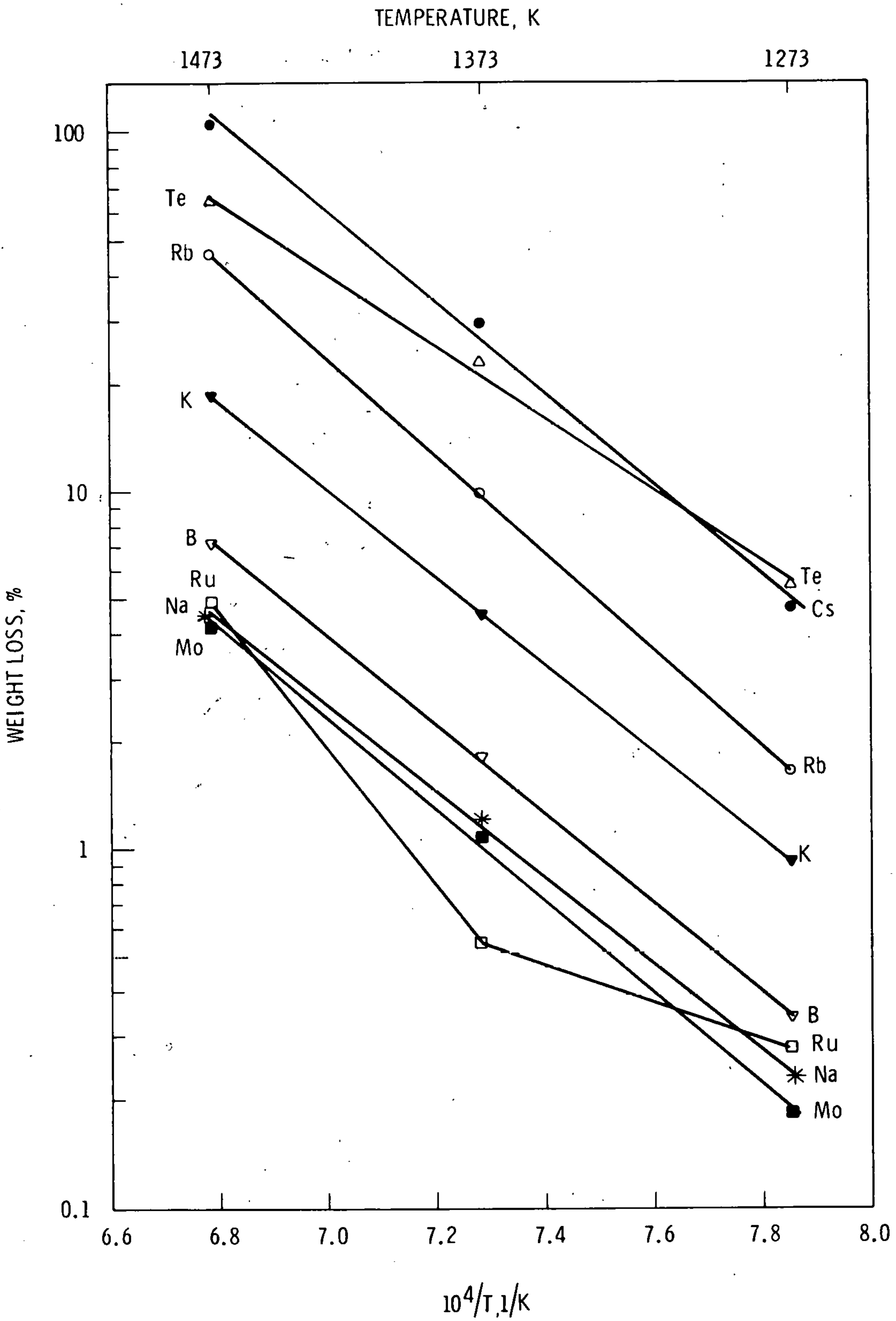

FIGURE 5.3. Loss of Elements from 72-68 Glass After 4 hr in Dry Air

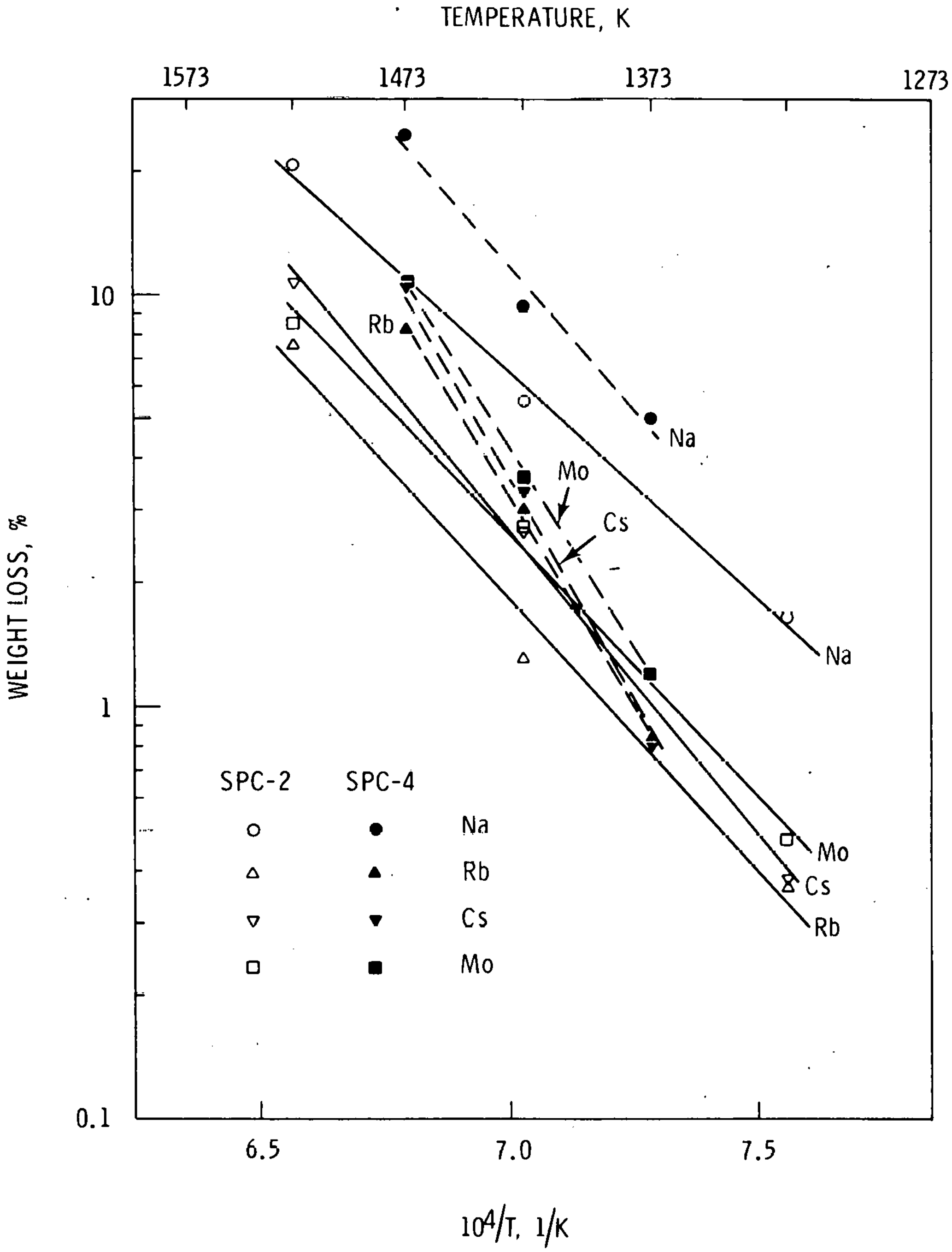

FIGURE 5.4. Loss of Elements from Supercalcine After 4 hr in Dry Air

5.2.3 Correlation with Viscosity

A reasonably good correlation between volatility and viscosity for glasses studied at PNL is shown by the data in Table 5.3 and Figure 5.5. Less viscous glasses tend to vaporize at higher rates. Data in Figure 5.5 are from a generic study that is described in more detail in Section 5.2.4. Other factors besides viscosity, such as concentration of the vaporizing species in the glass, affect vaporization, so the correlation is not perfect. However, it is good enough to suggest that the rate-limiting vaporization mechanism might be a gross mechanical process, such as fluid flow resulting from convection currents.

5.2.4 Composition Dependence

The five glasses for which data are presented in Figure 5.2 are quite similar in composition. They can all be characterized as borosilicate glasses with composition differences involving only relatively minor changes in the concentration of Na_2O, Al_2O_3, SiO_2, Fe_2O_3, ZnO, and RE_2O_3. Not surprisingly, their vaporization behaviors are similar. Even the two supercalcines, which are markedly different in composition and are ceramics rather than glasses, have weight losses not much different from the glasses. The different slopes, however, for the two supercalcines are surprising. Besides differences in the

TABLE 5.3. Volatility and Viscosity at 1323 K

Material	Volatility[(a)] g/m^2	Viscosity[(b)] Pa • s
72-68	50	3.6
76-183	33	12.5
77-260	30	9.5
76-68	17	19.0

(a) Taken from Figure 5.2.

(b) Data presented by G. B. Mellinger et al. at the American Ceramic Society meeting, Detroit, Michigan (1978), PNL-SA-6673.

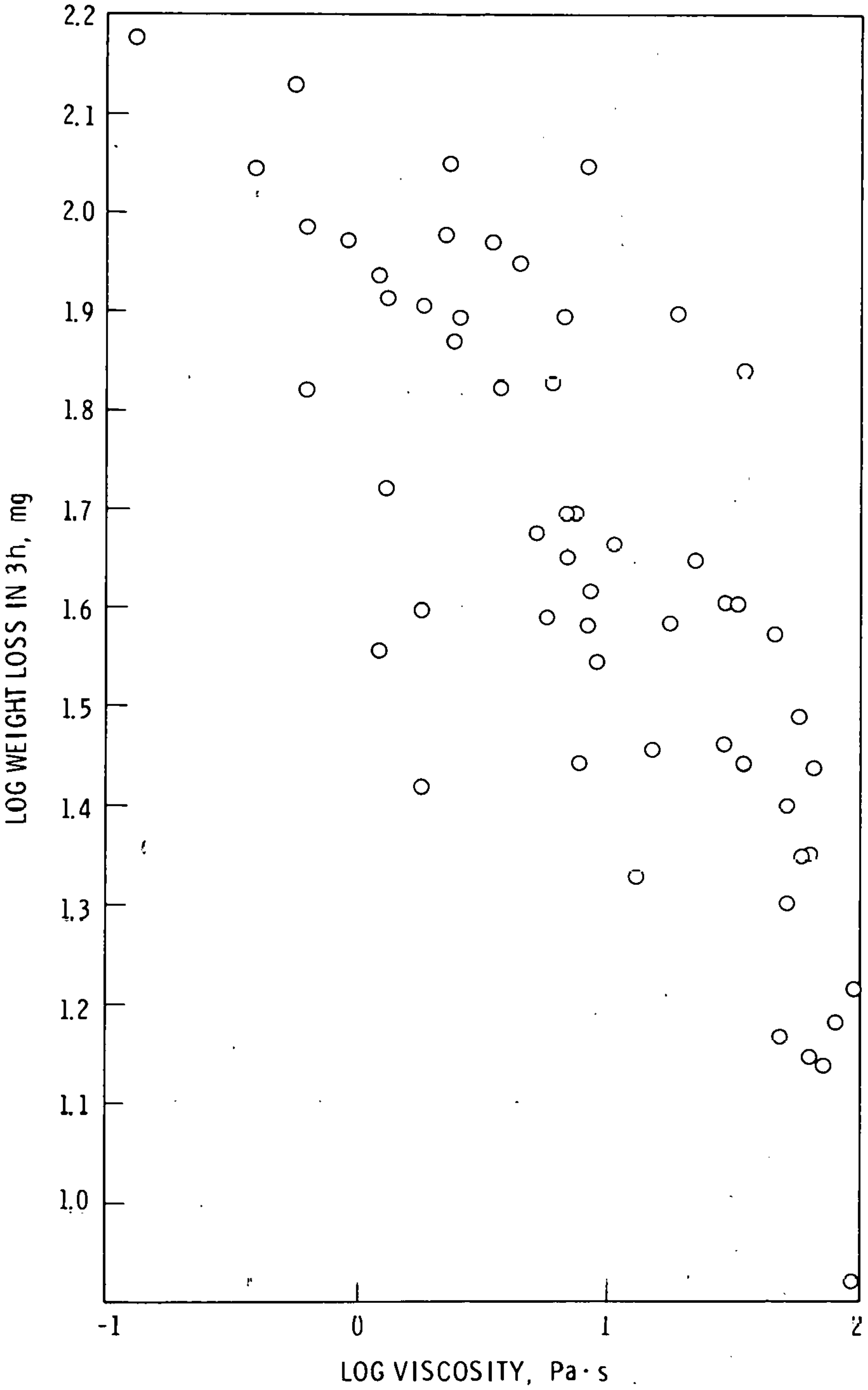

FIGURE 5.5. Viscosity (at 1250°C) Versus Volatility (at 1300°C) in Generic-Study Glasses

composition of the rare-earth oxides between SPC-2 and SPC-4, only the amounts of SiO_2, CaO, and SrO differ, and even these differences are only slight. Nevertheless, these composition differences are enough to cause differences in the relative amounts of two of the eight major crystalline phases present in the supercalcines (McCarthy et al. 1979; McElroy 1979). Efforts to correlate vaporization behavior with the differences in the crystalline phases have not been particularly successful (Gray 1980).

A separate generic study designed specifically to examine the effects of composition on properties of an 11-component glass system has been conducted at PNL (Chick et al. 1980). Fifty-six test compositions were chosen for study from the test matrix listed in Table 5.4. Fifty-five of the test compositions were selected from the corners (extreme vertices) of the test matrix, and one

TABLE 5.4. Generic Study Test Matrix

Oxide	Study Values, mole%		
	Low	Centroid	High
Formers			
SiO_2	41	49.7	60
B_2O_3	5.5	9.1	15
Al_2O_3	0	7.2	16
Modifiers			
Na_2O	9	12.7	17
MgO	0	3.9	9
CaO	0	6.7	14
Intermediates			
ZnO	0	3.0	6.5
TiO_2	0	3.4	8
Cr_2O_3	0	1.4	3.5
Fe_2O_3	0	1.5	3.5
NiO	0	1.4	3.5

54 mole% $\leq$ sum of formers $\leq$ 80 mole%

13 mole% $\leq$ sum of modifiers $\leq$ 35 mole%

test composition was that of the centroid composition. Property data were fit with a partial quadratic approximation model that was used to predict properties for other glasses with compositions within the field shown in Table 5.4. The predicted effects of composition changes on vaporization are illustrated in Figure 5.6. A weight loss of about 40 mg is plotted for the centroid composition where the lines intersect. Each line shows the predicted change in vaporization as the concentration of the corresponding component is changed from its centroid concentration. Standard prediction deviations were computed for each mole-percent change in component concentration, and the largest and smallest of these are shown on the plot as bars representing ±1 standard deviation. Changes or differences on the plot smaller than ±2 or 3 standard prediction deviations are considered insignificant.

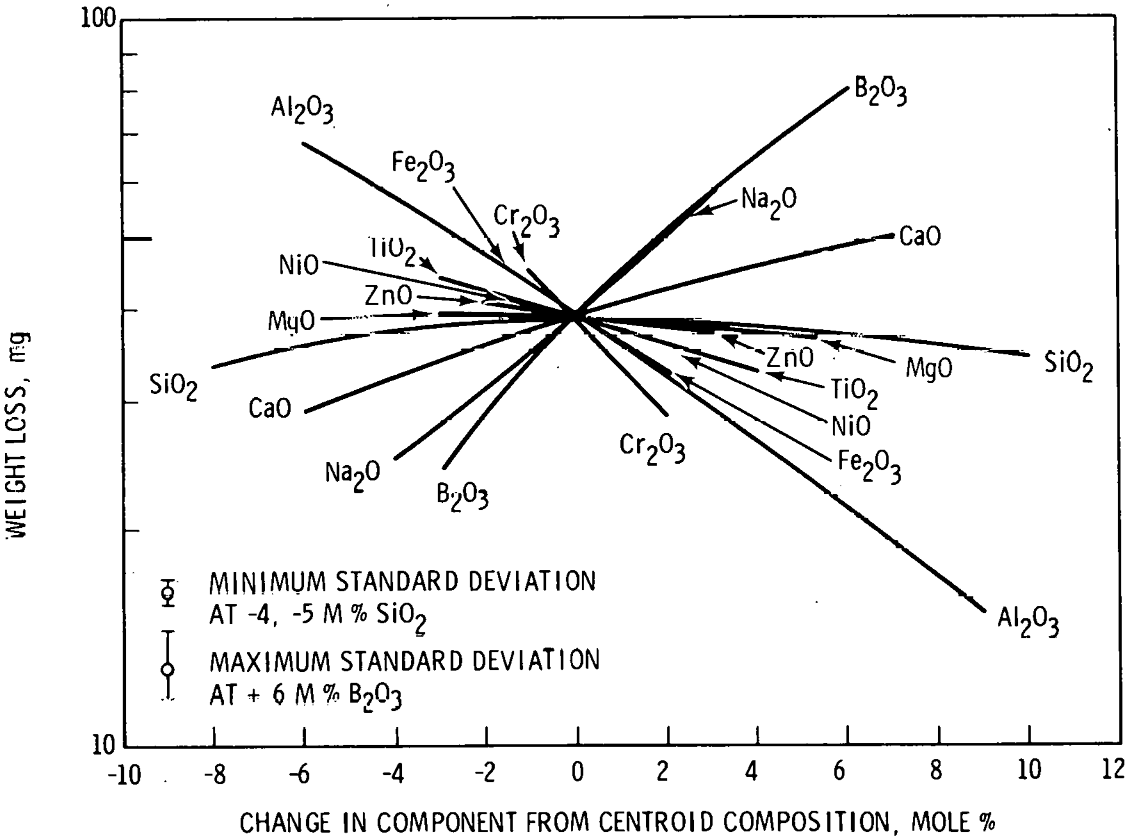

FIGURE 5.6. Effects of Components on Vaporization After 3 hr at 1300°C

The predicted results in Figure 5.6 show that increasing the Na_2O or B_2O_3 concentrations from the centroid composition increases vaporization and, conversely, decreasing their concentrations decreases vaporization. This is to be expected since, as discussed in Section 5.2.6, sodium and boron are the only elements that vaporize in measurable quantities. Thus, increasing their concentrations should accelerate vaporization. Understanding the effects of the other components is related to the correlation between viscosity and vaporization illustrated in Figure 5.5 and discussed in the preceding section. Any component that reduces viscosity when added to the glass would be expected to speed vaporization. Cr_2O_3, Fe_2O_3, and Al_2O_3 were found to increase viscosity the most strongly and therefore would be expected to decrease vaporization. SiO_2 increases viscosity only slightly, and Figure 5.6 shows it has little effect on vaporization. Adding Na_2O to the glass decreases viscosity; therefore, increasing Na_2O concentration would be expected to increase vaporization both because of its effect on viscosity and because it is a component of the vapor. CaO slightly decreases viscosity and slightly increases vaporization. All other components have little or no effect on vaporization.

5.2.5 Effect of Moisture on Vaporization Rate

A moist atmosphere usually, but not always, speeds the vaporization of glasses. The vaporization of simple silica-based glasses containing Na_2O is reported to be increased by this reaction (Sanders and Haller 1977):

$$H_2O(g) + Na_2O(\ell) \rightarrow 2NaOH(g) \qquad (1)$$

Figure 5.7 shows the effect of moisture on the only glass vaporized in a moist atmosphere at PNL. The mechanism of increased vaporization here probably includes the reaction (Terai and Kosaka 1976)

$$H_2O(g) + B_2O_3(\ell) \rightarrow HBO_2(g) \qquad (2)$$

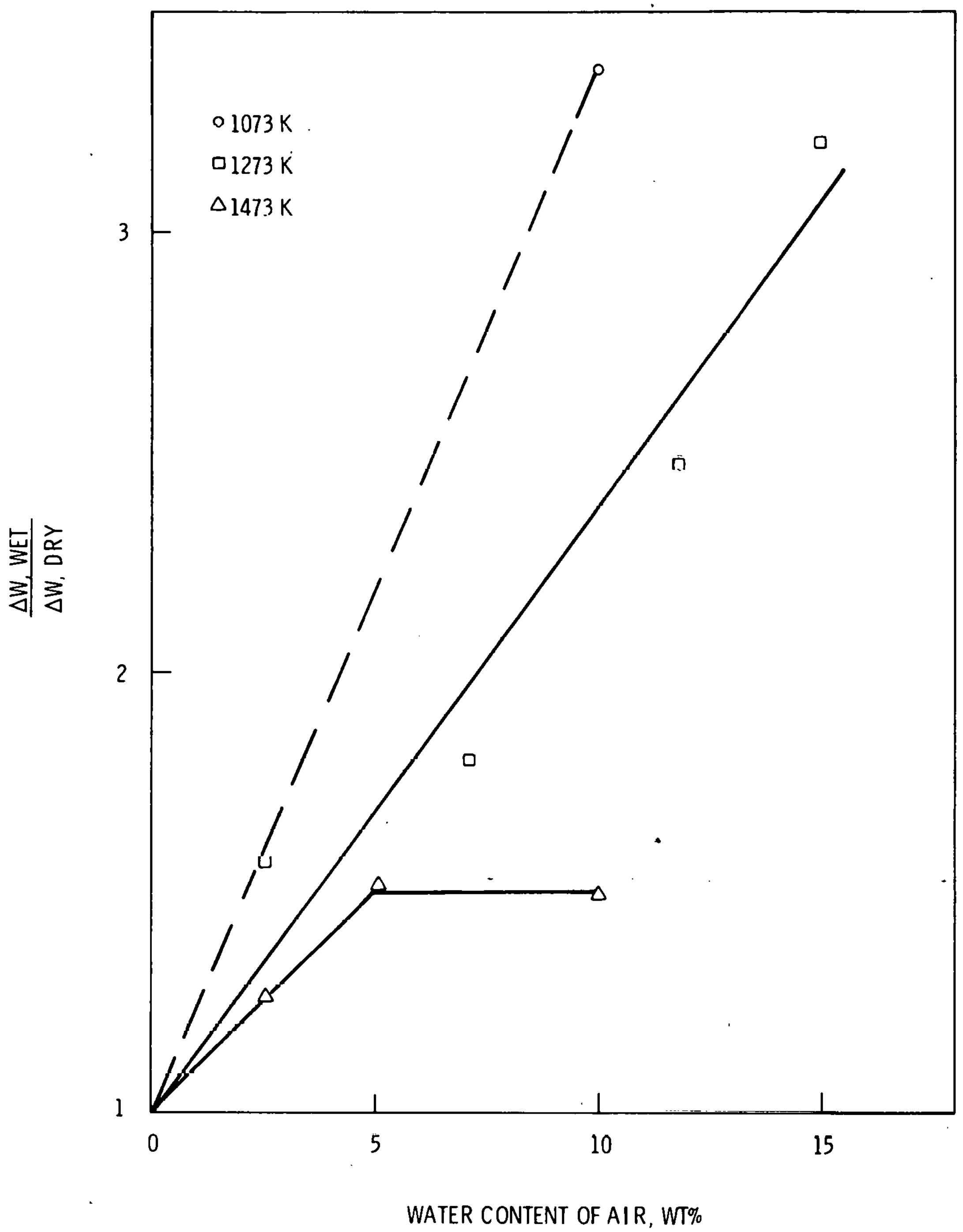

FIGURE 5.7. Effect of Moisture on Weight Loss from 72-68 Glass in 4 hr

since the vaporization of boron (and molybdenum) increased substantially. Reaction 1 probably is not operative for this glass because the vaporization of the alkali elements was either decreased by the moisture or was unaffected (Gray 1980).

As with other aspects of vaporization, seemingly modest composition differences result in marked differences in the effect of a moist atmosphere. For example, Walmsley, Sammons, and Grover (1969) used air with up to 15 wt% moisture and found a factor of three increase in vaporization of a phosphate glass but no effect on a borosilicate glass when both were vaporized at 1200°C. The composition of Walmsley's borosilicate glass, a simulated waste glass, was similar to the 72-68 glass studied at PNL except that it contained no zinc; 72-68 glass contained 21.6 wt% ZnO.

5.2.6 Composition of Vaporized Material

In terms of radioactivity released, cesium is the most volatile element. On a fractional release basis from the glasses, however, tellurium is about equally volatile (Figure 5.3). Molybdenum's vaporization is about equal to that of cesium in the supercalcines, while sodium's is higher than either (Figure 5.4).

Cesium apparently vaporizes from borosilicate glasses as metal or oxide, whereas the lighter alkali elements tend to vaporize as a borate. The major evidence for this is the data of Wilds (1978a), who used a Knudsen cell and a mass spectrometer to study vaporizing species from a borosilicate glass. He reported $NaBO_2$ and small amounts of $LiBO_2$, (Li,Na) BO_2, Na_2BO_2, and B_2O_3 but only elemental cesium, no cesium borates. Terai and Kosaka reported that potassium can vaporize as either $K_2O \cdot B_2O_3$ or $2K_2O \cdot B_2O_3$ (1976). In the PNL generic study mentioned earlier, the Na/B ratio in the vapor was always unity, even though the amount of B_2O_3 in the glass ranged from 6 to 12 mole% and the amount of Na_2O varied from 11 to 16 mole% (Chick et al. 1980). In results obtained on simulated wastes at PNL, the molar ratio (Na+K)/B in the vapor was about unity in one case, and in another case the ratio (Na+K+Rb+Cs)/B was approximately unity. But in other cases, no simple correlation between the amount of boron and alkalis in the vapor was apparent.

The supercalcines exhibit a lower cesium vaporization than the glasses because chemicals have been added to the supercalcines to produce pollucite, which is a stable cesium-containing compound. In only one case was an attempt made to reduce vaporization of cesium by altering a glass composition. Various amounts of TiO_2 were added to 76-183 glass because of reports that indicated TiO_2 additions decrease the vaporization of cesium, at least during the initial glass-melting process (Wilds 1978a and 1978b; Rudolph et al. 1972; Kelley 1975). Results, however, for the already-fabricated glass in Figure 5.8 show that additions of TiO_2 actually increased the vaporization of cesium. It is not known whether this discrepancy with the earlier reports results from the different glass compositions or if it reflects a difference between the initial and subsequent melts.

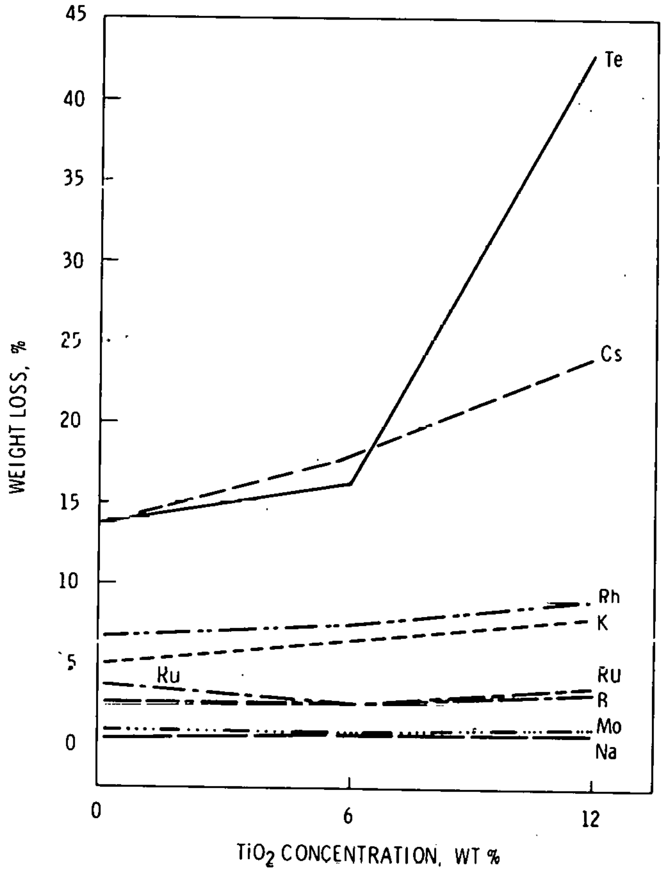

FIGURE 5.8. Effect of TiO_2 Concentration on Loss of Elements from 76-183 Glass After 4 hr in Dry Air at 1373 K

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6.0 RADIATION EFFECTS

W. J. Weber and F. P. Roberts

Radiation effects on the stability of high-level nuclear waste (HLW) forms are an important consideration in the development of technology to immobilize high-level radioactive waste because such effects may significantly affect the containment of the radioactive waste. Since the required containment times are long (10^3 to 10^6 years), an understanding of the long-term cumulative effects of radiation damage on the waste forms is essential. Radiation damage of nuclear waste forms can result in changes in volume, leach rate, stored energy, structure/microstructure, and mechanical properties. Any one or combination of these changes might significantly affect the long-term stability of the nuclear waste forms. This report defines the general radiation damage problem in nuclear waste forms, describes the simulation techniques currently available for accelerated testing of nuclear waste forms, and reviews the available data on radiation effects in both glass and ceramic (primarily crystalline) waste forms.

6.1 BACKGROUND ON RADIATION EFFECTS

This section discusses the sources of radiation effects in high-level nuclear wastes and the various state-of-the-art simulation techniques currently available for accelerated testing of the different waste forms.

6.1.1 Sources of Radiation Effects in Nuclear Waste Forms

The chief sources of radiation in the high-level nuclear waste forms are beta decay of the fission products (primarily cesium and strontium) and alpha decay of the actinide elements (uranium, neptunium, plutonium, americium, and curium). Spontaneous fission of some of the actinide isotopes and alpha-neutron reactions are sources of fission fragments and neutrons, but these radiation sources can generally be ignored because of their low production rates. Projected numbers of beta, alpha, and neutron events per metric ton of heavy metal for a commercial high-level waste are shown in Figure 6.1 for storage times up to 10^6 years (Roberts, Turcotte, and Weber 1981). In

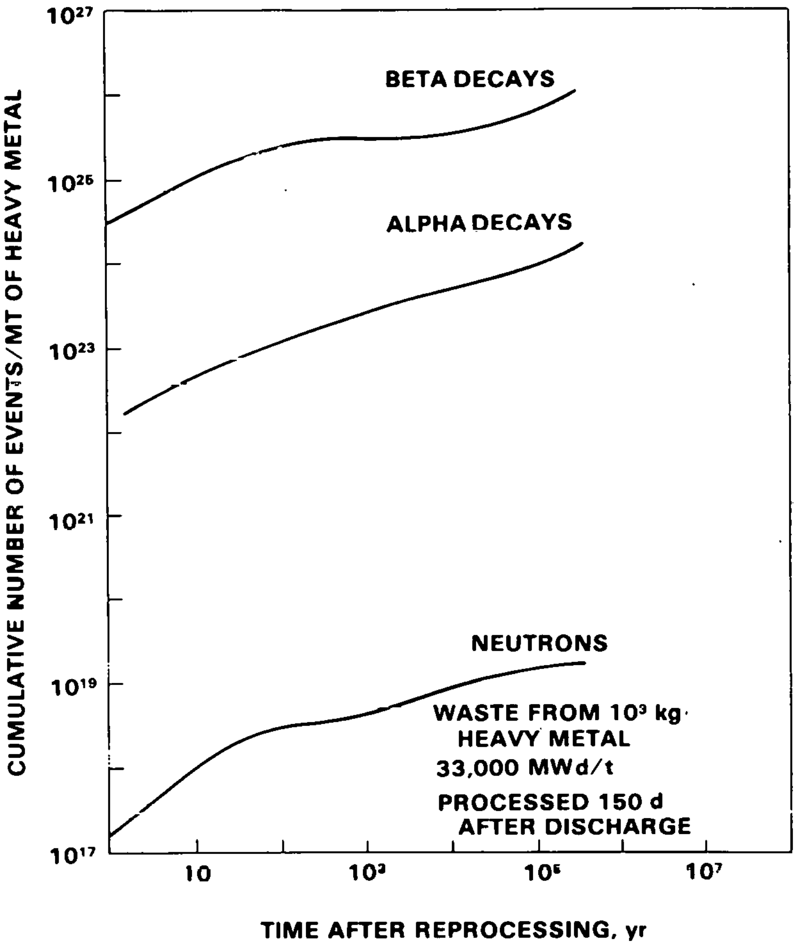

FIGURE 6.1. Cumulative Doses for a Commercial High-Level Waste (Roberts, Turcotte, and Weber 1981)

general, beta decay of the fission products predominates during the first 500 years with high radioactivities and high waste-form heat generation, while alpha decay predominates at longer times with a much lower heat generation rate.

Radiation damage in the waste forms is primarily produced by 1) the displacement of waste-form constituent atoms from their normal sites by elastic collisions of the nuclear projectiles with the atoms, 2) ionization effects, and 3) the transmutation of radioactive parent nuclei into different elements. These effects are discussed in the following two sections as related to the radiation sources (i.e., beta decay and alpha decay).

6.1.1.1 Effects of Beta Decay

Beta decay produces high-energy beta particles and gamma radiation that interact with the entire waste form solid primarily by ionizing processes and produce very few direct atomic displacements. From collision theory, beta particles are estimated to produce on the order of one displacement per decay event, and gamma radiation is relatively unimportant in displacement production (Roberts, Turcotte, and Weber 1981; Jenks and Bopp 1973). Displacements can also be produced in ionic solids by ionization, the principal interaction mode of beta particles and gamma radiation with solids. The electronic excitations caused by ionization can be localized (as separated or associated electron-hole pairs) and persist for sufficiently long times that the lattice becomes unstable and produces permanent ion displacements, a process often referred to as radiolysis (Hobbs 1976). In this manner, substantial displacement damage can be produced by ionizing radiation in those ionic solids where this mechanism is efficient (halides, hydrides, and azides). However, numerous ionic solids (mostly oxides) do not exhibit this effect, and it has not been established experimentally that this mechanism does occur in any of the waste forms currently under consideration.

The effects of ionization from beta-gamma interaction with the waste form solids include covalent bond rupture, valence changes, H_2O and OH^- decomposition (an important consideration for waste forms with a high water content), and decomposition of unstable molecular ions. Additionally, a radiation-induced change in the leach rate can result from radiolysis of the atmosphere and ground water in the presence of the intense ionizing radiation field (beta-gamma) associated with beta decay. Radiolysis of air or nitrogen in the presence of water can result in the formation of nitric acid (Jones 1959). Water radiolysis may result in the formation of various reactive-free radical and ionic species as well as hydrogen peroxide (Burns and Moore 1976; Draganic and Draganic 1971).

Another potential source of radiation-induced changes is the transmutation of the fission products. The two main sources of transmutations are the intermediate-lived fission products, ^{137}Cs (30.2 years half-life) and ^{90}Sr (28.1 years half-life), which undergo the following decay schemes:

$$^{137}\text{Cs} \rightarrow \, ^{137m}\text{Ba} + \beta^- \rightarrow \, ^{137}\text{Ba}$$

$$^{90}\text{Sr} \rightarrow \, ^{90}\text{Y} + \beta^- \rightarrow \, ^{90}\text{Zr} + \beta^- .$$

Transmutations can involve valence changes and major changes in atomic radii. Glass waste forms are more likely to tolerate these changes because they already have 10 to 25 elements present, including substantial concentrations of barium and zirconium. The crystalline phases in ceramic waste forms have ordered structures and are less likely to accommodate these kinds of changes.

6.1.1.2 Effects of Alpha Decay

Alpha decay results in the formation of two particles: a high-energy alpha particle (~4-6 MeV) and a recoil nucleus (~0.1 MeV). Nearly all the energy of the recoil nucleus is lost through elastic collisions with the waste form constituent atoms, producing several thousand atomic displacements. The alpha particle, on the other hand, dissipates most of its energy by ionization but still undergoes enough elastic collisions to produce several hundred atomic displacements. It is generally assumed that the primary source for radiation damage in nuclear waste solids is from displacement damage. Since alpha decay produces several orders of magnitude more displacements than any other radiation source as illustrated in Figure 6.2, most of the studies on radiation effects in waste solids have emphasized alpha decay effects.

The ionization dose from the alpha particles is significant and may exceed the ionization dose from beta-gamma radiation as illustrated in Figure 6.3 for commercial high-level waste. Consequently, all the ionization effects discussed in the previous section also apply for alpha particles. These effects (ionization-induced displacements, covalent bond rupture, valence changes, and water and air radiolysis) may also be significant as related to displacement damage; however, experimental evidence at this time tends to suggest that displacement damage dominates.

In complex ceramic waste forms, where the crystal size is small (0.1 to 10 μm), the alpha particles, which have a range of ~20 μm, effectively bombard

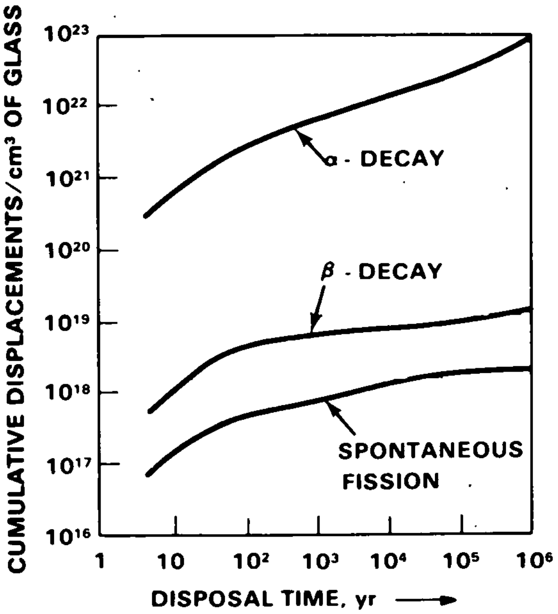

FIGURE 6.2. Cumulative Atomic Displacements in Commercial High-Level-Waste Solid (Roberts, Turcotte, and Weber 1981)

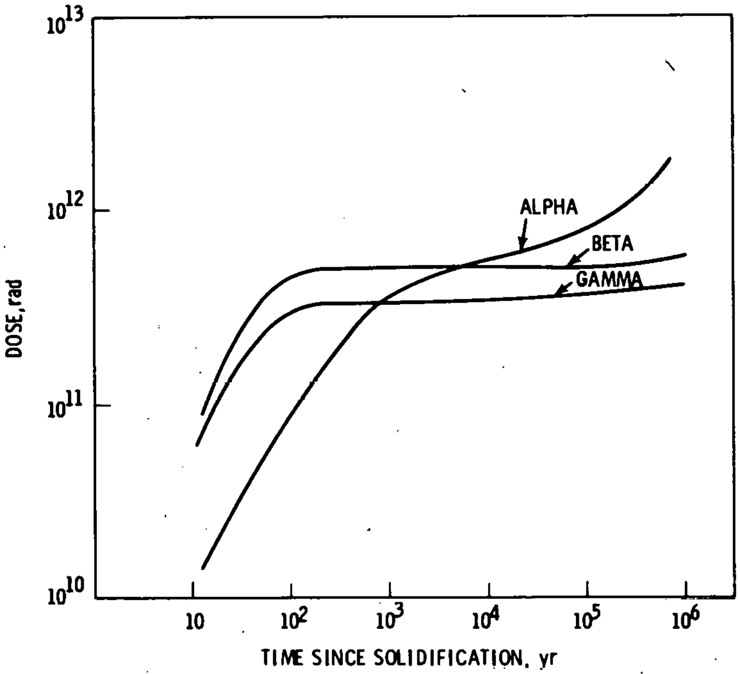

FIGURE 6.3. Sources of Ionizing Radiation Doses in Solidified Commercial High-Level Wastes from LWR Fuel Reprocessing. Burnup 33,000 MWd/MTHM; 5-Year cooling prior to reprocessing and solidification; 170 kg solidified waste/MTHM.

the entire solid, including the nonactinide-containing phases; the damage from the recoil nuclei, however, because of their short range (~0.01 μm), is confined to the phase in which the actinides are chemically incorporated. Consequently, alpha decay actually results in two related but different damage mechanisms: alpha-recoil damage (i.e., damage resulting from the synergistic effect of both alpha particle and recoil nucleus) in the actinide host phases and alpha particle damage in the nonactinide-containing phases.

Transmutation effects from the alpha decay of the actinides are generally ignored because the relatively few events produce only modest compositional changes over very long times.

6.1.2 Simulation Techniques

The effects of radiation on nuclear waste solids are produced by the decay of radioactive waste species contained within the waste form. The radiation damage accumulates over the decay time of these radioactive species and thus occurs over a period of hundreds to a million or more years. Laboratory experiments to test the radiation stability of proposed nuclear waste forms must, therefore, be accelerated simulation experiments. This section reviews the simulation techniques now being used to obtain data on the radiation stability of nuclear waste solids.

6.1.2.1 Actinide Doping Techniques

The long-term effects of alpha decay in nuclear waste forms can be effectively simulated in the laboratory by incorporating a short-lived actinide isotope, such as ^{238}Pu (87.7 years half-life) or ^{244}Cm (18.1 years half-life), in either a simulated waste form or the proposed actinide host phase (or phases) and allowing it to damage by self-radiation. This technique accurately reflects the long-term damage from alpha decay in the proposed waste forms. The technique is the basis for the test procedure drafted by the International Standards Organization (ISO) as a Standard Method for Testing the Irradiation Stability of Solidified Radioactive Waste (ISO/DIS 6962). The Materials Characterization Center (MCC) in the United States has also proposed a standard test procedure (MCC-6) based on actinide doping for accelerated testing of alpha decay effects.

6.1.2.2 Neutron Irradiations

Neutron irradiations take three different approaches, all involving in-reactor irradiations, to induce radiation damage in nuclear waste forms. One approach is to irradiate the test specimens of the proposed waste forms in a fast-neutron flux of a research reactor (Roberts, Jenks, and Bopp 1976; Reeve et al. 1980, 1981). The fast neutrons undergo elastic collisions with atoms in the waste solid, producing energetic primary knock-on atoms that undergo further elastic collisions as they slow down, resulting in numerous displacements. It is argued that the resultant displacement damage correlates with the damage from alpha decay, particularly the displacement damage from the recoil nuclei; however, such correlations are never easily made or easily interpreted. The method is simple and produces only moderately radioactive samples; however, it does have two disadvantages that must be considered:

- As no alpha particles are produced in this approach, there is no simulation of effects of helium atom deposition in the structure or any synergistic effect of the alpha particle damage with the recoil nucleus damage.
- In multiphase waste forms, all phases will experience the same fast neutron dose; whereas, in reality, some phases will contain no actinides and, therefore, will not experience recoil nuclei damage. These nonactinide-containing phases will be subject only to beta-gamma radiation and to alpha particles, which originate in the actinide-containing phases.

Another neutron irradiation technique (Antonini, Lanza, and Manara 1979) involves doping the waste form with ^{235}U (oxide) and irradiating test specimens in the neutron flux (thermal or fast) of a reactor. Such irradiation causes the ^{235}U to fission, producing high-energy fission fragments, which cause displacements. This method provides a less accurate simulation of alpha decay damage than does fast neutron irradiation, and correlation of the damage to alpha decay damage is difficult, if not impossible, as recently pointed out by Weber (J. Nucl. Mater., in preparation). This technique also results in highly active specimens that must be stored for some time to allow sufficient radioactive decay before examination.

The third technique (Malow and Andresen 1979) involves utilizing the high ^{10}B (n,α) cross section for slow neutrons. Boron-containing or boron-doped waste forms are irradiated in the slow-neutron flux of a reactor, producing alpha particles (E_{max} = 1.78 MeV). High rates of helium formation are possible, and borosilicate glasses require no actual boron doping. A major disadvantage is that the damage produced is not completely equivalent to alpha-recoil damage.

6.1.2.3 Charged-Particle Irradiations

Charged-particle irradiations with electrons, protons, alpha particles, or heavy ions (Ni, Pb) offer a technique for simulating radiation damage in very short times without the difficulties associated with handling radioactive materials. The results, however, are difficult to interpret because the effects are concentrated in a narrow surface layer and in a small area, making post-irradiation analysis more difficult. The assumptions behind these methods are as follows:

- All the energetic particles, including high-energy electrons ($E > 0.5$ MeV), produce displacement damage that probably can be correlated with the displacement damage from alpha decay.
- Heavy-ion irradiation should simulate the damage from recoil nuclei.
- Alpha bombardment, particularly with alphas emitted by an actinide source, provides a realistic simulation of irradiation effects due to alpha particles in the nonactinide-containing phases.
- High-energy electron irradiations (>0.5 MeV) can simulate high-energy beta damage. Low-energy electron irradiations (<0.5 MeV) cause only ionizing damage, which can simulate beta-gamma ionization effects.

The first two assumptions are difficult to completely justify because correlation of damage produced by different particles is never straightforward, and irradiation damage from a single particle type may be quite different from the real case, where the synergistic effects of all the radiation species are included. The last two assumptions are more easily justified for the specific cases indicated; post-irradiation analysis, however, is still limited because of the small volume irradiated.

6.1.2.4 Gamma Irradiations

The effects of gamma radiation on the properties of nuclear waste forms or on leach rate (due to radiolysis of the atmosphere and ground water surrounding the waste form) are most effectively and accurately simulated by performing irradiation testing in a gamma-radiation facility that incorporates a ^{60}Co source. Dose rates on the order of 2.5 x 10^6 R/hr are easily obtainable, and in some facilities dose rates of ~10^7 R/hr are achievable with some heat generation.

6.1.2.5 Transmutation Simulation

Techniques for simulating transmutation effects in nuclear waste forms are limited. At present, only one experimental procedure has been utilized to study transmutation effects. In this technique (Chick et al. 1980; Weber, Wald, and Gray 1980), nuclear waste forms and selected single-phase materials are neutron-irradiated to convert a large fraction (~12% in that study) of the natural ^{133}Cs to ^{134}Cs, which then transmutes to ^{134}Ba with a 2.06-year half-life. Immediately after irradiation, the materials are annealed to remove the neutron damage, and changes in waste form properties are then monitored as a function of the transmutation ingrowth.

6.1.3 Radiation Damage in Natural Minerals

Another approach to help understand the complex effects of radiation damage in nuclear waste forms, particularly crystalline waste forms and their proposed actinide host phases, is by evaluating radiation damage in natural minerals. Radiation damage in natural minerals results from the alpha decay of the uranium and thorium nuclides incorporated within the crystal structure. The damage in the minerals manifests itself in several ways, such as the formation of fission tracks, pleochroic halos, and metamict minerals (Ewing 1981).

Most of the interest in this area has centered on the metamict minerals, particularly those that are isostructural or structurally similar to proposed actinide host phases in crystalline waste forms. Metamict substances are those which were originally crystalline but have become amorphous. Although the mechanism for loss of crystallinity in these minerals is not clearly understood, damage caused by the decay of the uranium and thorium nuclides is certainly critical in metamictization. Comparison of metamict and nonmetamict polymorphs, such as thorite and huttonite ($ThSiO_4$), may provide a basis for understanding the susceptibility of different crystal structures to radiation damage (Ewing and Haaker 1980).

In recent years, several synthetic mineral types have been proposed as ideal hosts for actinides in nuclear waste ceramics, such as the supercalcine and SYNROC formulations, based on the apparent radiation and chemical stability of the closely related natural minerals over a wide range of geologic and geochemical environments. Many of these natural mineral analogues are only relatively stable with respect to radiation damage and often tend toward metamictization over long geologic time. The modification of the chemistry of the synthetic minerals in actual high-level waste ceramics may make some of these actinide host phases more susceptible to radiation damage.

In general, the natural mineral analogues of proposed actinide host phases in nuclear waste ceramics provide only qualitative information about the radiation stability of the proposed synthetic mineral phases. The available information on these natural analogues is often incomplete or inconsistent on such aspects as age, weathering, and change in leach rate as a result of metamictization. Clearly, the testing of radiation damage in simulated waste forms containing these proposed synthetic minerals is needed to conclusively demonstrate the structural and chemical stability of these phases to radiation damage.

6.2 RADIATION DAMAGE IN GLASS WASTE FORMS

Glass is a highly developed solid form for the storage of high-level nuclear wastes (Mendel 1978). As a result, most of the studies of radiation damage, both in the United States and abroad, have concentrated on proposed glass waste forms. The experimental results to date on the effects of radiation damage on volume, leach rate, stored energy, structure/microstructure, and mechanical properties of glass waste forms are reviewed below. Much of the data represents radiation damage effects produced by alpha decay in actinide doped waste forms, since it is generally assumed that this mechanism is the primary source for radiation damage in nuclear waste forms (Section 6.1.1.2).

There also exists a large volume of radiation effects data for earlier work on glass for other applications; this information is not included in this report. Primak (1977), however, has recently reviewed some of the data on radiation effects in simple glasses pertinent to the development of nuclear waste glasses. Reviews of extensive early work on radiation damage in glass are also available (Gilmour and Heenan 1965; Riley, Coppins and Duckworth 1958).

6.2.1 Volumetric Changes

The volume (or density) of high-level nuclear waste glasses can decrease, increase, or remain unchanged as a result of radiation damage. Volume changes can cause internal stresses in the waste glass, particularly in partially devitrified glass if differential volume expansions occur, and can also lead to possible strains in the metal canister. Almost all the data on radiation-induced volume changes in nuclear waste glasses have been obtained in actinide doping studies of alpha decay damage. There is also a very limited amount of data from neutron-induced fission damage and from electron irradiations.

6.2.1.1 Actinide Doping

Several waste glass compositions have been studied at the Pacific Northwest Laboratory (PNL) using the actinide-doping technique described in Section 6.1.2.1 (Mendel et al. 1976; Mendel et al. 1977; Ross et al. 1978; Ross and Mendel 1979; Weber et al. 1979). The compositions of these waste glasses are given in Table 6.1, along with the concentration of the actinide dopant ($^{244}Cm_2O_3$). One glass composition (PNL 77-260) was prepared in three initial forms: one vitreous and two partially devitrified (Weber et al. 1979). One of the partially devitrified glass forms (slow-cooled at 6°C/hr from 1050°C) contained large crystals (~25 to 100 μm), and the other (700°C, 1 week) contained a fine dispersion of small crystals (<5 μm). The change in density as a function of accumulated dose was measured. The density measurements were

TABLE 6.1. Composition of PNL Simulated High-Level Waste Glasses

COMPONENT	72-68-a	72-68b	76-68	76-260	E-G	P-G
	Weight Percent of Component					
Glass Components						
SiO_2	27.0	27.0	38.8	34.9	50.6	23.4
B_2O_3	11.0	11.0	9.2	8.7	12.7	7.3
Li_2O	--	--	--	--	4.0	--
Na_2O	4.0	4.0	7.3	7.8	5.1	2.8
K_2O	8.0	4.0	--	1.9	--	2.8
TiO_2	--	--	2.9	5.8	--	--
CaO	1.5	1.5	1.9	1.0	2.6	--
MgO	1.5	1.5	--	--	--	--
SrO	1.5	1.5	--	--	--	--
BaO	1.5	1.5	--	--	--	--
Al_2O_3	--	--	--	1.9	--	--
ZnO	21.0	21.0	4.9	--	--	--
PbO	--	--	--	--	--	38.0
CuO	--	--	--	2.9	--	--
Fission Products						
Rb_2O	0.22	0.22	0.12	0.10	0.22	0.22
SrO	0.65	0.65	0.36	0.26	0.65	0.65
Y_2O_3	0.02	0.02	0.20	0.15	0.02	0.02
ZrO_2	3.04	3.04	1.70	1.33	3.04	3.04
MoO_3	3.91	3.91	2.17	1.73	3.91	3.91
RuO_2	1.82	1.82	1.02	0.76	1.82	1.82
Rh_2O_3	0.30	0.30	0.17	0.14	0.30	0.30
PdO	0.91	0.91	0.51	0.44	0.91	0.91
Ag_2O	0.05	0.05	0.03	0.02	0.05	0.05
CdO	0.05	0.05	0.03	0.03	0.05	0.05
TeO_2	0.45	0.45	0.25	0.19	0.45	0.45
Cs_2O	1.77	1.77	0.99	0.70	1.77	1.77
BaO	0.96	0.96	0.54	0.49	0.96	0.96
La_2O_3	1.97	--	0.51	0.40	1.97	1.97
CeO_2	3.98	--	1.15	0.81	3.95	3.95
Pr_6O_{11}	0.41	--	0.51	0.39	0.41	0.41
Nd_2O_3	1.40	--	1.60	4.13	1.40	1.40
Sm_2O_3	0.25	--	0.32	0.01	0.25	0.25
Eu_2O_3	0.06	--	0.07	0.05	0.06	0.06
Gd_2O_3	0.17	--	0.05	0.03	0.17	0.17
Actinides						
U_3O_8	--	--	4.39	4.67	--	--
Cm_2O_3	1.0	0.2	3.0	3.0	1.0	1.0
Others$^{(a)}$						
Na_2O	--	--	4.84	2.81	--	--
Fe_2O_3	0.93	0.93	9.38	1.08	0.93	0.93
Cr_2O_3	0.21	0.21	0.40	0.02	0.21	0.21
NiO	0.09	0.09	0.20	0.01	0.09	0.09
P_2O_5	0.41	0.41	0.46	2.08	0.41	0.41
MnO_2	--	--	--	0.09	--	--
Gd_2O_3	--	--	--	9.11	--	--
ZrO_2	--	--	--	0.12	--	--

(a) Includes corrosion products, nuclear poisons, process chemicals, and cladding residues.

made on ~3-g test specimens by the buoyancy technique. The density changes (percent) as a function of accumulated dose for these waste glass compositions are shown in Figure 6.4. The glasses either expanded (density decrease) or contracted (density increase), depending on composition. The density changes tend to follow an exponential behavior as a function of dose, as described by the following relation:

$$\Delta\rho/\rho = A[1 - \exp(-BD)] \tag{1}$$

where ρ is the density of the glass, D is the dose (alpha decays/cm^3), and A and B are material-dependent parameters (A is the density change at saturation

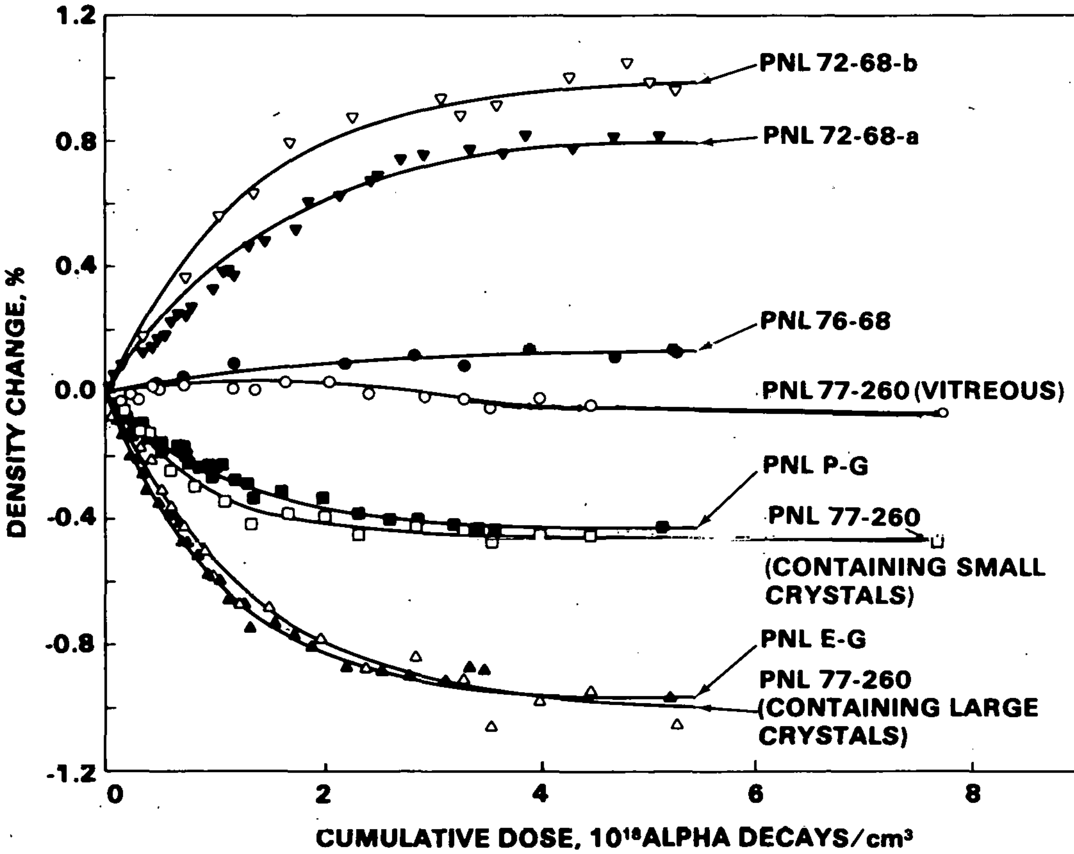

FIGURE 6.4. Density Changes in ^{244}Cm-Doped Waste Glasses (Roberts, Turcotte, and Weber 1981)

and B determines the rate of density change). The values of A and B, as determined by regression analyses of the data, for the different waste glasses are given in Table 6.2. From the results, the volumetric changes in these waste glasses should not exceed approximately ±1%; a volume change on this order can be tolerated by present canister designs (Mendel 1978).

Bibler and Kelley (1978) have evaluated the effects of internal alpha decay on the density of a borosilicate glass (52.5 wt% SiO_2, 10 wt% B_2O_3, 22.5 wt% Na_2O, 10 wt% TiO_2, and 5 wt% CaO) for long-term storage of Savannah River Plant (SRP) radioactive waste. Two glasses, each containing 45 wt% of a simulated dry waste [50 mole% $Fe(OH)_3$ and 50 mole% MnO_2], were prepared by actinide doping. One was doped with 0.49 wt% ^{244}Cm, and the other with 0.97 wt% ^{238}Pu. A third glass, containing no simulated waste, was also prepared by doping with 0.81 wt% ^{238}Pu. Measurements were made over a period of 420 days to an accumulated dose of ~1.2 x 10^{18} alpha decays/cm^3 for the ^{244}Cm-doped glass and ~6 x 10^{17} alpha decays/cm^3 for the ^{238}Pu-doped glasses. Density measurements (performed at 22 ±1°C by weighing in air and carbon tetrachloride) of all three glasses showed a volume expansion that increased linearly with dose over the range studied. The maximum volume change observed

TABLE 6.2. Values of Constants A and B, for Exponential Dependence of Density Change in PNL Glasses (adapted from Roberts 1980)

PNL Glass Composition	A[(a)]	B, cm^3
72-68-a	8.33×10^{-3}	6.7×10^{-19}
72-68-b	10.0×10^{-3}	7.7×10^{-19}
76-68	1.33×10^{-3}	5.3×10^{-19}
77-260 (vitreous)	not measurable	not measurable
77-260 (small crystals)	-4.5×10^{-3}	11.0×10^{-19}
77-260 (large crystals)	-10.2×10^{-3}	6.6×10^{-19}
E-G	-9.75×10^{-3}	8.7×10^{-19}
P-G	-4.36×10^{-3}	9.3×10^{-19}

(a) Predicted density change at saturation.

(^{244}Cm-doped glass) is about 0.55%. Since the changes in volume in all three glasses show no signs of approaching saturation, larger volume expansions can be expected at higher doses. (Data at higher doses have not been reported.) The two waste glasses containing simulated waste and doped with ^{244}Cm or ^{238}Pu are very similar in their rates of volume change with dose. In the glass containing no simulated waste and doped with ^{238}Pu, the rate of volume change with dose was significantly less than in the other two glasses that contained simulated waste.

In a collaborative program to characterize waste forms undertaken by the Centre de Marcoule (CEA-France), the Hahn-Meitner Institut (Berlin), and the Atomic Energy Research Establishment (Harwell, UK), four borosilicate glasses and one phosphate glass were doped with $^{238}PuO_2$, and the effects of radiation damage studied (Malow, Marples, and Sombret 1980). The four borosilicate glasses, designated SON 58.30.20.U2 (French), VG 98/3 (German), UK-209 and UK-189 (British), were doped with 2.5 wt% $^{238}PuO_2$. The Pamela phosphate glass was doped with 5 wt% $^{238}PuO_2$ because of the higher solubility of PuO_2 in this glass. The changes in density as a function of accumulated dose in these glasses are shown in Figure 6.5. The Pamela phosphate glass and the French glass, SON 58.30.20.U2, show an increase in density with dose (volume contraction), while in the other three borosilicate glasses the density decreases (volume expansion). All the glasses are showing signs of saturation in density change and fit the exponential relation given by Eq. 1. The values of the constants, A and B, for these glasses are given in Table 6.3. The results predict that the volume expansion for three of the glasses will saturate at less than 1.0%, while the volume contraction of SON 58.30.20.U2 will saturate at about 1.2%. The values of B for these glasses are smaller than the values of B for the PNL glasses (Table 6.2). This indicates that the European glasses will saturate at a slightly slower rate (per unit dose) and, hence, higher dose than the PNL glasses.

Two other studies on the effects of alpha decay on glass volume have also been carried out. At Harwell, Hall et al. (1976) measured length changes in a borosilicate glass developed to immobilize Magnox fuel reprocessed waste and

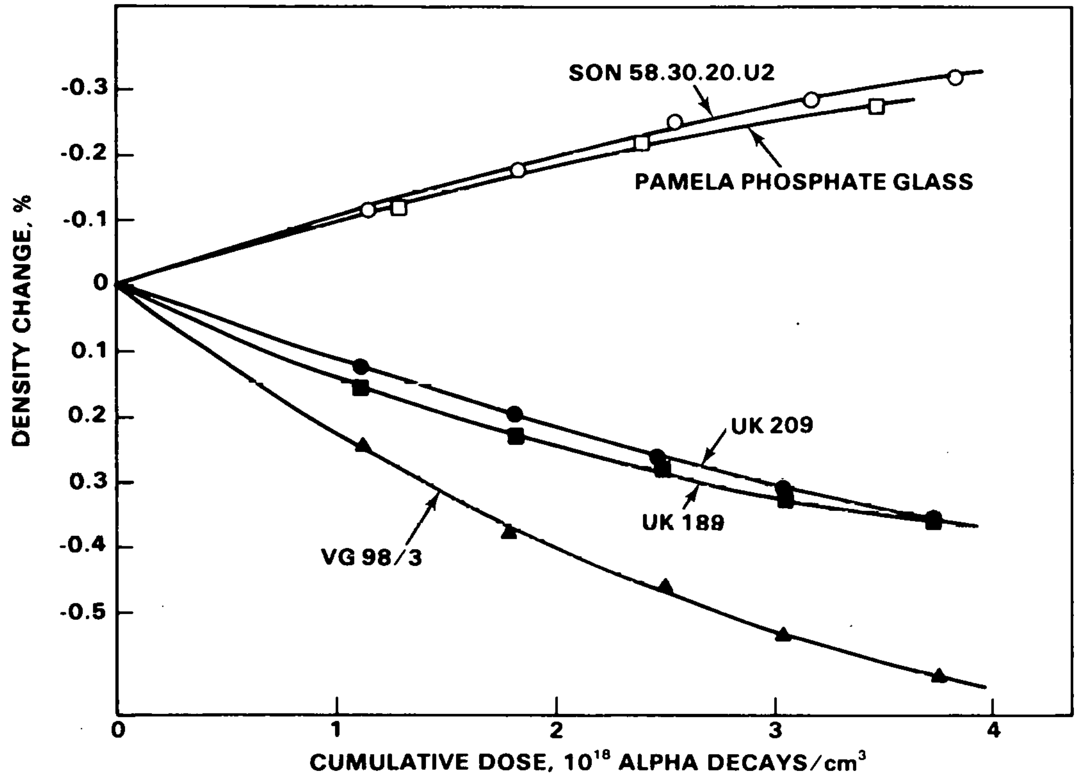

FIGURE 6.5. Density Changes in ^{238}Pu-Doped European HLW Glasses (adapted from Malow, Marples and Sombret 1980)

TABLE 6.3. Values of Constants A and B for Exponential Dependence of Density Change in European Glasses (adapted from Malow, Marples and Sombret 1980)

Glass Composition	A(a)	B, cm^3
SON 58.30.20.U2	12.0×10^{-3}	3.5×10^{-19}
VG 98/3	-8.8×10^{-3}	1.3×10^{-19}
UK-209	-9.0×10^{-3}	1.0×10^{-19}
UK-189	-4.9×10^{-3}	3.0×10^{-19}

(a) Predicted density change at saturation.

doped with 5 wt% $^{238}PuO_2$. At 50°C storage temperature, the length increased by 0.02% after 2 x 10^{18} alpha decays/cm^3; whereas, in specimens stored at 170°C the length increased by 0.4% after 0.27 x 10^{18} alpha decays/cm^3 and then slowly decreased with dose. Unfortunately, initial density measurements were not made; therefore, density data is not available as a function of dose. After a dose of 2 x 10^{18} alpha decays/cm^3, the specimens were annealed and density recovery measured. The specimens stored at 50°C showed a 0.15% increase in density after heating to 460°C, while the specimens stored at 170°C exhibited a decrease in density of 0.23% after heating to 480°C. The disparity between the dilatometer and density measurements was not resolved. In the other study, Bonniaud et al. (1979, 1980) observed no density changes in either a ^{241}Am doped glass or a ^{238}Pu doped glass after ~1 x 10^{18} alpha decays/cm^3.

6.2.1.2 Neutron Irradiations

Uranium doping followed by neutron irradiation has been used in a simulation experiment by Antonini et al. (1980) to study density changes as a function of displacements per atom (dpa) in a borosilicate glass representative of the glasses commonly taken into consideration in Europe for high-level waste vitrification. They doped samples of the borosilicate glass waste form with different amounts of ^{235}U, encapsulated test specimens in a cadmium shield to eliminate the thermal neutrons and irradiated the specimens in the high-flux reactor at Petten to induce damage by the fissioning of the ^{235}U (Antonini, Lanza and Manara 1979). The specimens were irradiated to doses ranging from 0.0012 dpa (1 x 10^{15} fissions/cm^3) to 0.36 dpa (4 x 10^{17} fissions/cm^3), reported to represent equivalent alpha-decay doses of ~3 x 10^{16} alpha decays/cm^3 to 9.4 x 10^{18} alpha decays/cm^3, respectively. Density measurements were carried out in hot cells by the traditional Archimedian method using tetrachloroethylene (density = 1.67 g/cm^3) as the reference fluid. The results show a definite decrease in density (volume expansion), but the functional dependence of density change on dose is uncertain due to large scatter in the data. The maximum volume expansion measured was 0.80%. (Note: There is an error in the dose values given in Table 1 of Antonini et al. 1980; the last two dose entries should be increased by a factor of 10.)

6.2.1.3 Charged-Particle Irradiations

Hall et al. (1976) simulated radiation damage from beta decay in simulated Magnox waste glass by irradiating with 0.5-MeV electrons from a Van de Graaff accelerator. The irradiations were carried out at 300°C to a dose of 10^{19} electrons/cm^2 (~2.5×10^{11} rad). Density measurements revealed no significant volume change.

6.2.1.4 Gamma Irradiations

There have been no gamma irradiation experiments performed on glass waste forms that measured volumetric changes. Shelby (1980), however, has measured density changes in several commercial borosilicate glasses irradiated with ^{60}Co gamma radiation over the dose range from 10^8 to 10^{11} rad. The radiation-induced densification increased with dose and apparently with boron content. The maximum volume change observed was ~1.0%.

6.2.1.5 Transmutation Simulation

As discussed previously (Section 6.2.2.5), there is currently only one transmutation simulation experiment being carried out. In that study (Chick et al. 1980; Weber, Wald and Gray 1980), three glasses are being studied: A simulated waste glass, a high-cesium glass, and a high-silica glass. The high-cesium glass was prepared in two forms, with and without ^{244}Cm (~2 wt%). Density measurements after about 3% of the total cesium transmuted to barium indicate no significant volume changes in either the simulated waste glass or the high-silica glass. The two forms of the high-cesium glass have both shown volume contractions of about 0.8%. This study is continuing, and future data should establish whether these trends continue.

6.2.2 Leach Rate Changes

The leach rate of a high-level nuclear waste solid is the rate at which the components of the waste form are attacked and dissolved by a contacting liquid and is, therefore, a measure of the chemical durability of the material. The leach rate of a waste form is important in geologic disposal because the primary pathway of radionuclide migration to the biosphere begins with ground water leaching of the waste form. Radiation damage may affect the leach rate by producing physical and chemical changes in the waste form or by producing chemical changes in the surrounding environment (mainly the ground water).

6.2.2.1 Actinide Doping Data

Of the several waste glass compositions doped with ^{244}Cm at the Pacific Northwest Laboratory (Table 6.1), only two of the compositions, PNL 72-68-a and 77-260, have been studied for changes in leach rate (Mendel et al. 1976; Mendel et al. 1977; Weber et al. 1979; Roberts 1980). Mendel et al. (1976 and 1977) measured the leach rate of curium-doped PNL 72-68-a as a function of time by a static leach test in distilled water at 25°C. The leach rates were determined from both potassium and curium in solution. The results, based on average values from seven different specimens, are shown in Figure 6.6 along with the leach rate (based on potassium) of a similarly prepared but undoped sample of PNL 72-68-a. The leach rates based on potassium are significantly higher (two orders of magnitude) than those based on curium. This suggests that curium leaches at a much lower rate than the more soluble alkali ions, such as potassium, or that the solubility of the curium in the solution is low enough to control the curium release rates. A comparison of the leach rates, based on potassium, of the curium-doped and undoped samples shows that the curium-doped sample has a slightly higher leach rate (factor of two) but does not significantly change with time (or dose). The difference between the doped and undoped samples may be a solution radiolysis effect from the alpha particles at the sample-solution interface in the curium-doped study. Similar behavior from gamma radiolysis has been reported by McVay and Pederson (1981) and McVay, Weber and Pederson (1980) and will be described in more detail below (Section 6.2.2.4). Roberts (1980) measured the leach rate change of PNL 72-68-a as a function of dose using the dynamic Soxhlet test described by Mendel et al. (1977). The leach rate, determined by weight loss, did not increase significantly (less than factor of two) as shown in Figure 6.7 after a dose of 10 x 10^{18} alpha decays/cm^3; this is a factor of two beyond where the structural damage saturated. The increase is well within the experimental error of the tests.

Weber et al. (1979) performed leach testing on three forms of PNL 77-260, one vitreous and two partially devitrified (see Section 6.2.1.1), using both

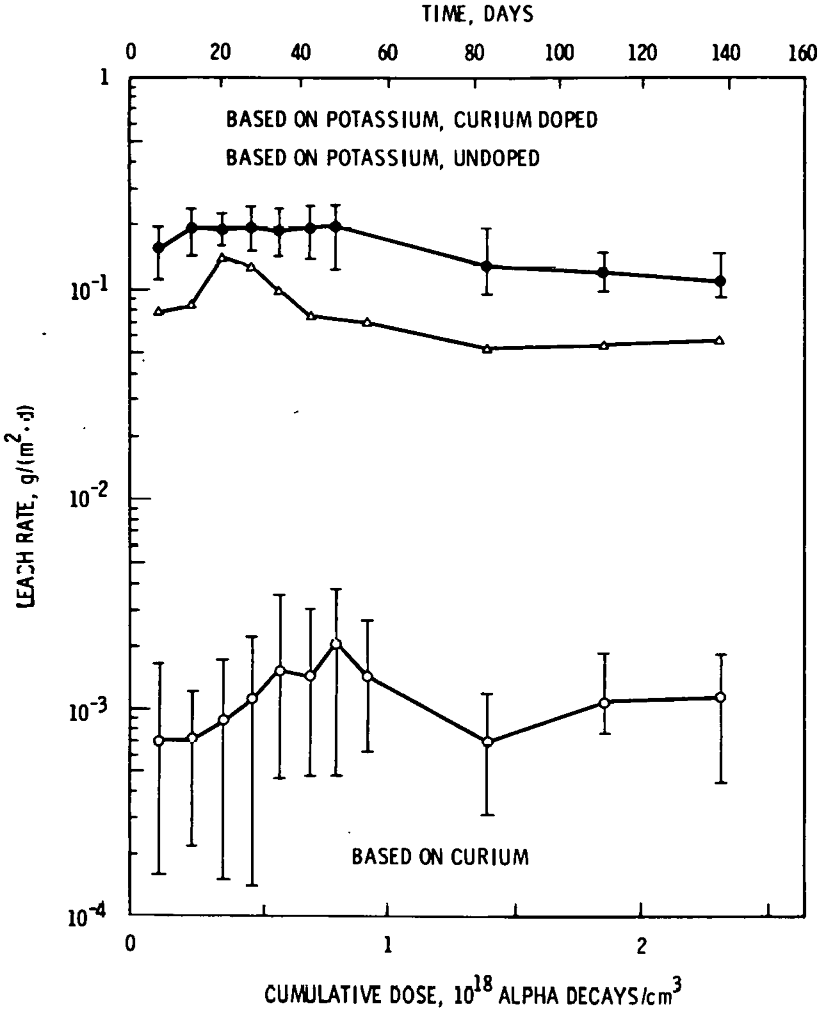

FIGURE 6.6. Static-Test Leachability at 25°C ^{244}Cm-Doped PNL 72-68-a (adapted from Mendel et al. 1976)

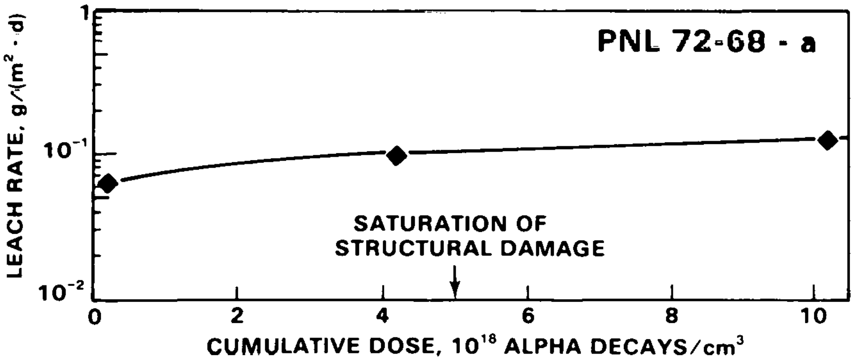

FIGURE 6.7. Soxhlet-Test Leachability of ^{244}Cm-Doped PNL 72-68-a HLW Glass (adapted from Roberts 1980)

dynamic Soxhlet and acid-base tests (Mendel et al. 1977). The leach rates calculated from both overall weight loss and from the ^{244}Cm concentration in the leachant are shown in Figure 6.8. The results obtained by weight loss were significantly higher than the results based on ^{244}Cm in solution, except in the pH 4 test, where the results are comparable. The amount of ^{244}Cm in solution increases as the leachant goes from basic (pH 9) to acid (pH 4), which directly follows the solubility behavior of actinides as a function of pH. The ^{244}Cm is apparently retained to a higher degree by the glass and devitrification products than the more soluble elements (alkali, boron), in agreement with the PNL 72-68-a results discussed above, but leach rates based on a single species in solution should be suspect. In general, the results based on weight loss are more indicative of actual behavior, and in the case of PNL 77-260 the results show no significant change in leach rate after a dose of 4.4×10^{18} alpha decays/cm^3, which is the dose where saturation of structural changes was nearly complete. The results also showed that amorphization of a crystalline phase within the two partially devitrified glasses did not significantly affect the leach rates.

In the study by Bibler and Kelley (1978) discussed in Section 6.2.1.1, the actinide leachabilities of the two ^{244}Cm- and ^{244}Pu-doped borosilicate glasses containing simulated radioactive waste were determined by leach testing in stirred, distilled water at 25°C (the leach water was changed daily). The leachabilities were calculated based on the measured alpha activity in the water. The calculated leachabilities did not significantly change with dose. The maximum dose attained was 1.1×10^{18} alpha decays/cm^3 in the ^{244}Cm-doped glass and 4.4×10^{17} alpha decays/cm^3 in the ^{238}Pu-doped glass. The leachability of the ^{238}Pu ($\sim 4.0 \times 10^{-4}$ g/m^2 • d) in the glass was consistently higher than for the ^{244}Cm ($\sim 0.5 \times 10^{-4}$ g/m^2 . d). This suggests that either the ^{244}Cm is more strongly bound in the matrix than is the ^{238}Pu, or the solubility of ^{244}Cm is less than the solubility of ^{238}Pu is in the solution. These results, however, provide data only on actinide leachability (or solubility) and, as discussed above, are not easily extrapolated to the actual leach rate (or change in leach rate) of the glass waste form being tested.

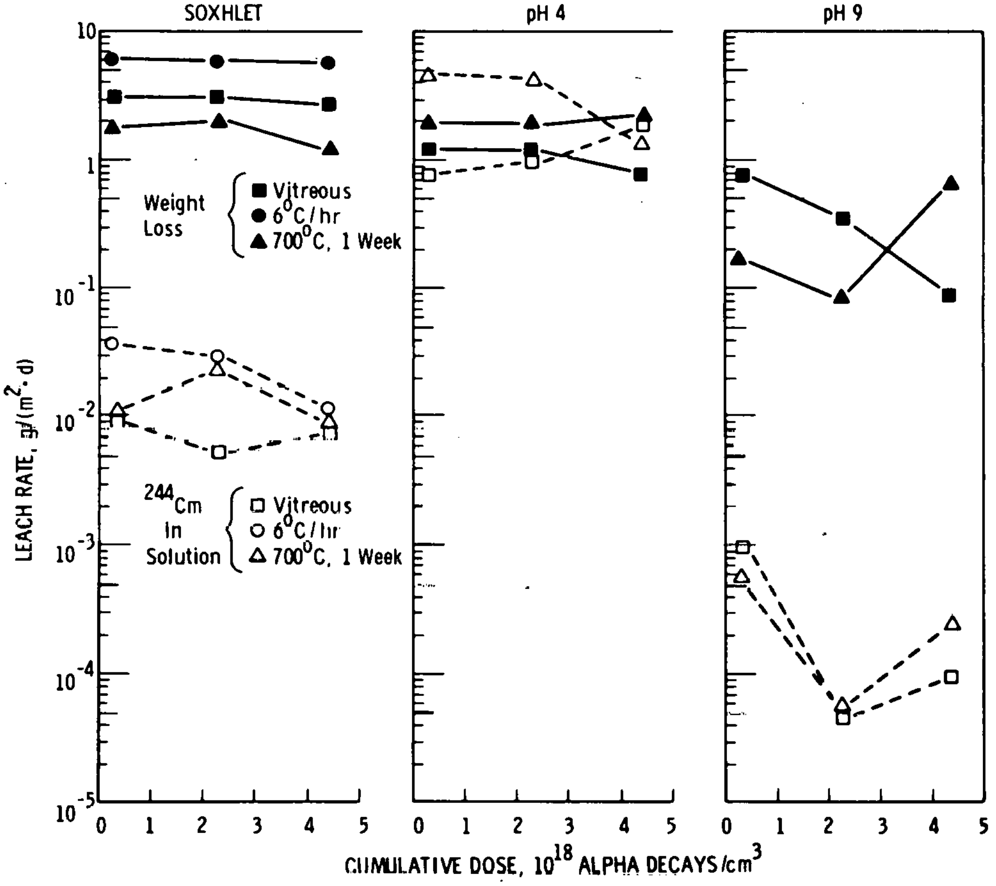

FIGURE 6.8. Leachability in ^{244}Cm-Doped PNL 77-260 HLW Glass (Weber et al. 1979)

Several studies of changes in leach rates of actinide-doped waste glasses have been carried out abroad. Bonniaud, Jacquet-Francillon, and Sombret (1980) measured the change in leach rate for a ^{244}Cm-doped glass, a ^{241}Am-doped glass, and a ^{238}Pu-doped glass by static leach test with tap water. The leach rates were calculated from the actinide activity of the leachant; consequently (as previously discussed), they are the leachabilities (or solubilities) of only the individual actinides and may not provide information on the actual leach rate changes of the glass. The data show little change in actinide leachability as a function of increasing dose. Scheffler and Riege (1977) also measured leach rate changes in a ^{242}Cm-doped borosilicate glass by static leach tests at 23°C. They observed no significant changes in leach rate with increasing dose up to a dose of ~4 x 10^{18} alpha decays/cm^3.

Boult et al. (1979) measured the change in leach rate of UK glass 189 doped with 5 wt% ^{238}Pu. Samples were stored at 20°C between the leach tests. The leach rates, based on weight loss, were measured by the Soxhlet leach test. Initial leach rates were not measured. The leach rate did increase by about 50% between 1 year (2.4×10^{18} alpha decays/cm^3) and 2 year (4.7×10^{18} alpha decays/cm^3) storage. No significant, further increases were observed after 3-year storage (7.1×10^{18} alpha decays/cm^3).

The most complete work on European glasses is the collaborative effort reported by Malow, Marples, and Sombret (1980) and referred to in Section 6.2.1.1. In that study, the leach rates were determined initially and after 3.3×10^{18} alpha decays/cm^3 by using the Soxhlet technique and calculated from the weight loss. Samples were stored at 50°C and 170°C during the self-radiation. The leach test results are given in Table 6.4. All the glasses show an increase in leach rate. The changes are not considered significant, except for SON 58.30.20.U2; in this glass, however, the alumina content, which improves leach resistance, was only one-tenth of that normally specified for this glass.

TABLE 6.4. Leach Rates Based on Weight Loss and Measured by the Soxhlet Technique for European HLW Glasses Doped with 2.5 wt% ^{238}Pu (adapted from Malow, Marples and Sombret 1980)

Glass	Storage Temp., °C	Initial Leach Rate, g/m^2 · d	Final(a) Leach Rate, g/m^2 · d
UK 189	50	13.3	19.1
UK 189	170	10.9	17.9
UK 209	50	2.1	2.3
UK 209	170	2.3	2.8
SON 58.30.20.U2	50	22.6	69.0
SON 58.30.20.U2	170	21.9	35.6
VG 98/3	50	22.1	29.1
VG 98/3	170	21.8	23.3

(a) Final leach rate measured after a cumulative dose of 3.3×10^{18} alpha decays/cm^3.

Most data on the change in leach rate in actinide-doped HLW glasses have been measured using the Soxhlet technique and calculated based on weight loss. In general, this has occurred because the Soxhlet technique gives fairly reproducible results, the calculations based on weight loss give a better indication of actual leach rates than calculations based on a single species in solution, and only changes in leach rates were of interest and not absolute values. All the data obtained by the Soxhlet technique on HLW glasses and discussed above are summarized in Table 6.5. This probably represents the best current state-of-the-art understanding of changes in leach rate due to radiation-induced changes in the chemical durability of HLW glasses. (This is to be distinguished from radiation-induced changes induced by radiolysis of the leachant discussed below.) The maximum change in leach rate is 205% (factor of 3), but in general, the increase in leach rate is less than 100% (factor of 2), and in some instances (PNL 77-260) small decreases in the leach rate are measured.

TABLE 6.5. Summary of Leach Rate Changes in HLW Glasses Obtained by the Soxhlet Technique and Based on Weight Loss

Simulated HLW Glass	Storage Temp., °C	Maximum Dose, alpha decays/cm^3	Leach Rate Change at Maximum Dose, %	Reference
PNL 77-260 (vitreous)	23	4.4×10^{18}	-10	Weber et al. 1979
PNL 77-260 (700°C, 1 wk)	23	4.4×10^{18}	-33	Weber et al. 1979
PNL 77-260 (6°C/hr)	23	4.4×10^{18}	-5	Weber et al. 1979
PNL 72-68-a	23	10.2×10^{18}	+100	Roberts 1980
UK 189	20[(a)]	7.1×10^{18}	+44	Boult et al. 1979
UK 189	20[(b)]	7.1×10^{18}	+73	Boult et al. 1979
UK 189	23	3.3×10^{18}	+44	Malow et al. 1980
UK 189	170	3.3×10^{18}	+64	Malow et al. 1980
UK 209	23	3.3×10^{18}	+10	Malow et al. 1980
UK 209	170	3.3×10^{18}	+22	Malow et al. 1980
SON 58.30.20.U2	23	3.3×10^{18}	+205	Malow et al. 1980
SON 58.30.20.U2	170	3.3×10^{18}	+63	Malow et al. 1980
VG 98/3	23	3.3×10^{18}	+32	Malow et al. 1980
VG 98/3	170	3.3×10^{18}	+7	Malow et al. 1980

(a) Stored at 50°C for 1 yr (2.4×10^{18} alpha decays/cm^3).
(b) Stored at 170°C for 1 yr (2.4×10^{18} alpha decays/cm^3).

6.2.2.2 Neutron Irradiation Data

There have been no neutron irradiation experiments reported to date on HLW glasses which measured irradiation-induced changes in leach rate. However, Rauscher and Tischer (1964) reported increased solubility of some commercial borosilicate glasses after neutron irradiation. The solubilities increased by no more than a factor of three after fluences of 1.4 x 10^{19} n/cm^2.

6.2.2.3 Charged-Particle Irradiation Data

Dran et al. (1980) have irradiated a simple borosilicate glass (64 wt% SiO_2, 12 wt% B_2O_3, and 24 wt% Na_2O) and several simulated European HLW glasses with low-energy (~1 KeV/amu) lead ions in an effort to quickly evaluate the effect of irradiation on leach rate. Their premise is that the low-energy lead ions simulate the recoil nuclei generated by alpha decay. Polished sections of the material to be irradiated are covered with an electron microscope grid and then exposed to the beam of lead ions. The result is a periodic succession of irradiated and unirradiated areas. The irradiated areas extend to a depth of ~50 nm (500 Å). The irradiated specimens are then leached in a NaCl solution (250 g/l) at 100°C. The change in leach rate due to irradiation is inferred from the difference of depth between the irradiated and unirradiated areas with a diamond stylus device (accuracy reported to be ~10 Å). Their results suggest irradiation-enhanced changes in leach rates on the order of factors of 25 to 500. Such increases in leach rate are in sharp contrast to the results from actinide decay (Section 6.2.2.1); however, the technique employed is open to question as to its ability to predict actual changes in bulk leach-rate behavior as a result of alpha decay. This is currently the subject of much debate, and questions concerning surface damage versus bulk damage and such effects as irradiation texturing of the surface, the small damage depth, the role of alpha particles (which are not present in the lead-irradiation studies), different leachants, dose rate, etc. will need to be answered by more fundamental studies before data from such studies of ion irradiation can be applied to the evaluation of nuclear waste forms.

Araki (1981) has reported irradiation studies of several Japanese simulated HLW glasses using 2-MeV electrons from a Cockcroft-Walton type accelerator to simulate beta-gamma damage. The irradiations were carried out to

~10^{10} rad, and no measurable changes in leach rates were observed. Bonniaud (1977) also performed electron irradiations on a number of HLW glasses using 3 MeV electrons at doses as high as 1.2 x 10^{11} rad. No changes were observed in the cesium or strontium leach rates.

6.2.2.4 Gamma Irradiation Data

Grover (1973) irradiated borosilicate and phosphate glasses in the Gamma Irradiation Facility at Mol to a dose of ~1 x 10^{11} rad over the temperature range from 350 to 800°C. For the borosilicate glass there was a slight increase in the leach rate (based on cesium and strontium in solution) between 600 and 650°C. There is a much larger increase in the leach rate (about a factor of 10) of the phosphate glass at temperatures above 550°C. In another study, Kelley (1975) irradiated two borosilicate waste glasses with gamma radiation from a ^{60}Co source to 10^{10} rad at ~65°C. No changes in leachabilities were observed. Mendel et al. (1977) also reported no significant changes in the leach rates of full-level borosilicate waste glasses after doses of 1 to 4.6 x 10^{11} rad.

In a different type of study, McVay and Pederson (1981) and McVay et al. (1980) reported significant increases in the leach rate of PNL 76-68 in the presence of ^{60}Co gamma radiation at a dose rate of 2.4 x 10^6 R/hr. Some of the increased leaching was due to the generation of nitric acid from air radiolysis in the leach vessel. Nitric acid appeared to preferentially attack zinc and lanthanides, both of which normally build up on the surface of the glass when leached in nonacidic solutions. Increased rates were also observed for samples irradiated while leaching, but with air excluded to eliminate nitric acid formation, which indicated that water radiolysis products may also be important. Samples irradiated with gamma radiation prior to leaching showed dissolution rates indistinguishable from those of unirradiated specimens. These results may explain the factor of ~2 higher leach rates observed by Mendel (1973) in waste glasses containing up to 90 Ci/cm^3 of fission products than in nonradioactive waste glasses of similar composition.

6.2.2.5 Transmutation Simulation Data

Data are not currently available on leach rate changes in the only transmutation simulation experiment currently under way (Chick et al. 1980; Weber, Wald and Gray 1980).

6.2.3 Stored Energy Changes

Stored energy is the latent energy stored in a glass matrix (or crystal lattice) by radiation, generally through the displacement of atoms. The stored energy is released as heat when the irradiated material is thermally annealed. Although stored energy is now generally believed to be unimportant in solid nuclear waste forms, an understanding of the amount of energy involved and of the annealing behavior is, however, useful for evaluation of the potential hazards. If the quantity of stored enerpy is large and the release rate high, an uncontrolled release could produce sudden excessively high waste-form temperatures. Such high temperatures could affect the physical and chemical properties of the waste forms and the integrity of the waste-form canister.

6.2.3.1 Actinide Doping Data

Radiation-induced changes in stored energy have been studied for several different waste-glass compositions doped with ^{244}Cm at the Pacific Northwest Laboratory (Mendel et al. 1976; Mendel et al. 1977; Mendel 1978; Roberts, Jenks and Bopp 1976; Roberts, Turcotte and Weber 1981; Ross et al. 1978; Turcotte and Roberts 1977; Weber et al. 1979). The stored energy release was measured by differential scanning calorimetry (DSC) on specimens weighing 25 to 60 mg at a heating rate of 20°C/min, as described in detail by Roberts, Jenks, and Bopp (1976). One of the PNL waste glass compositions (PNL 72-68) has been studied more extensively than any other glass composition in this country or abroad. The rates of energy release in PNL 72-68-a as a function of temperature and cumulative dose are shown in Figure 6.9 (Roberts, Jenks and Bopp 1976). The release occurs over a broad temperature range, and a two-stage release mechanism is suggested. The stored energies as a function of cumulative dose for PNL 72-68-a (1 wt% ^{244}Cm) and PNL 72-68-b (8 wt% ^{244}Cm) are shown in Figure 6.10 (Turcotte and Roberts 1977; Mendel et al. 1977); these results suggest that dose rate effects (factor of eight) are not significant.

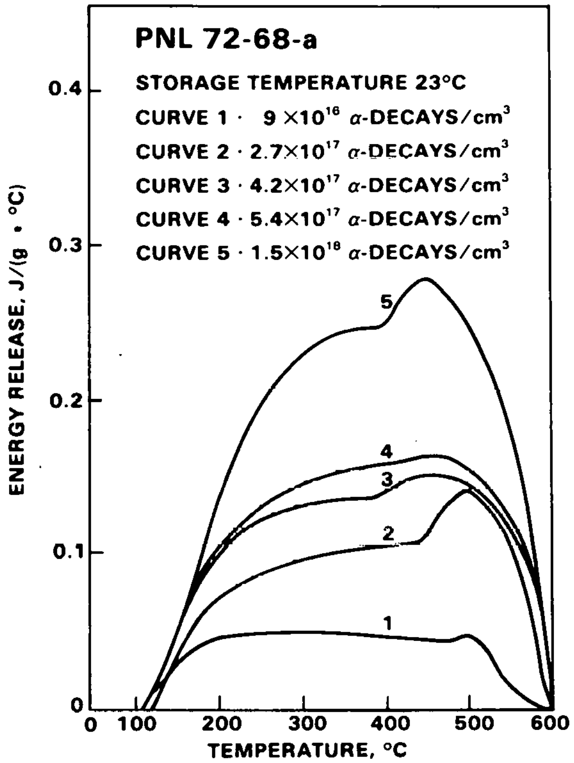

FIGURE 6.9. Stored Energy Release Rates in ^{244}Cm-Doped PNL 72-68-a HLW Glass (adapted from Roberts, Jenks and Bopp 1976)

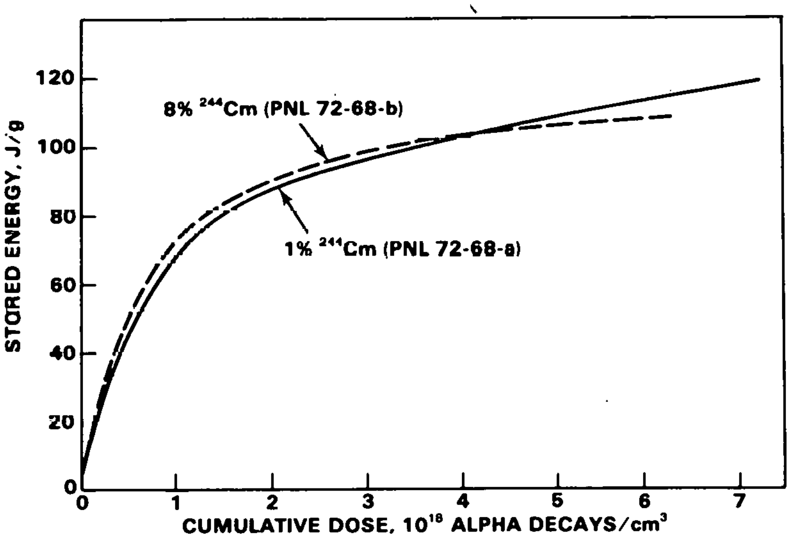

FIGURE 6.10. Effect of Dose Rate on Stored Energy in ^{244}Cm-Doped PNL 72-68 HLW Glass (adapted from Turcotte and Roberts 1977)

The stored energy of PNL 72-68-b as a function of cumulative dose (and equivalent storage time, assuming commercial HLW) at very high dose levels is shown in Figure 6.11 (Ross et al. 1978; Mendel 1978). The stored energy shows a maximum at a value of ~120 J/g. The effect of storage temperature on the buildup of stored energy in PNL 72-68-a is shown in Figure 6.12 for a cumulative dose of 1.7 x 10^{18} alpha decays/cm^3 (Roberts, Jenks and Bopp 1976). The results show that stored energy is inversely proportional to storage temperature and is completely absent in PNL 72-68-a when stored at 350°C.

The stored energies as a function of cumulative dose for all the PNL waste-glass compositions studied to date are shown in Figure 6.13 (Roberts, Turcotte and Weber 1981). In general, the buildup of stored energy follows exponential behavior similar to the change in density (Eq. 1) and saturates at a value in the range of 80 to 130 J/g. In the case of PNL 77-260, the vitreous form (data in Figure 6.13) exhibited a higher release rate than the two partially devitrified forms (data not shown), but this is attributed in part to volume effects and an insufficient temperature to anneal all the damage out of

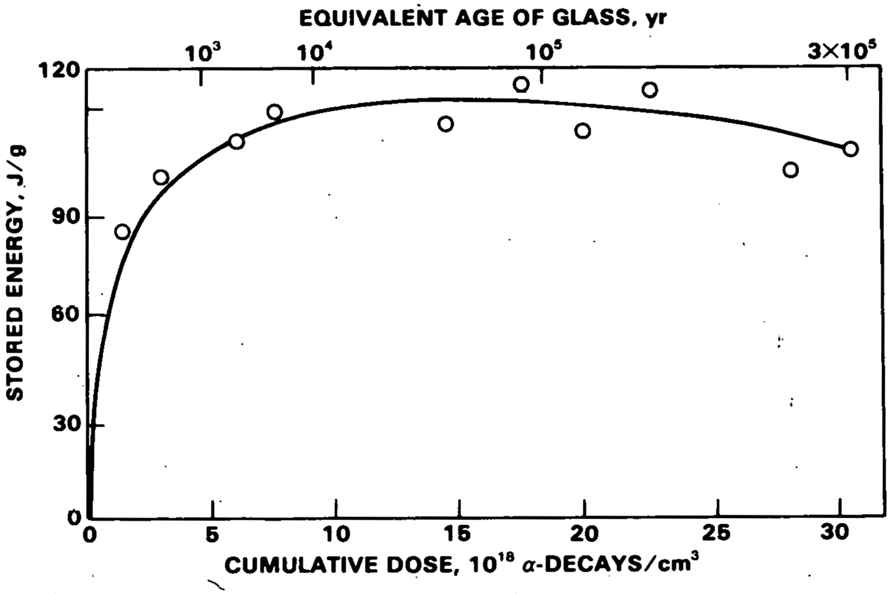

FIGURE 6.11. Stored Energy in ^{244}Cm-Doped PNL 72-68-b HLW Glass at Very High Doses (adapted from Mendel 1978)

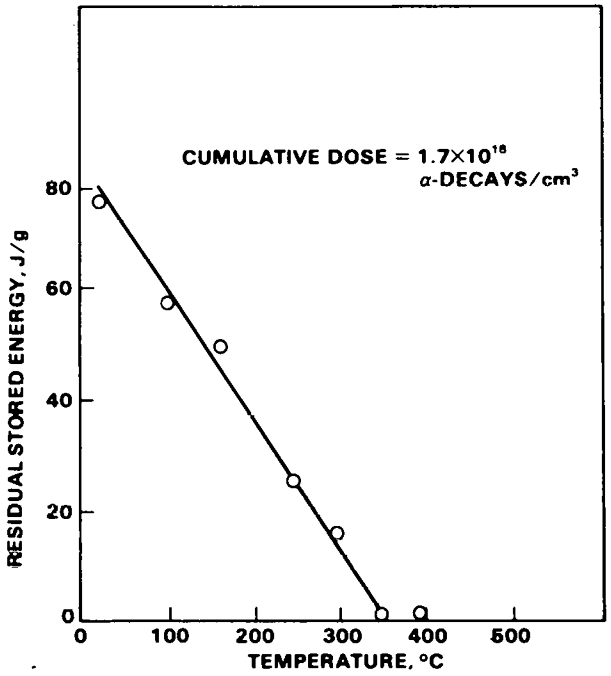

FIGURE 6.12. Effect of Storage Temperature on Stored Energy in PNL 72-68-a HLW Glass (adapted from Roberts, Jenks and Bopp 1976)

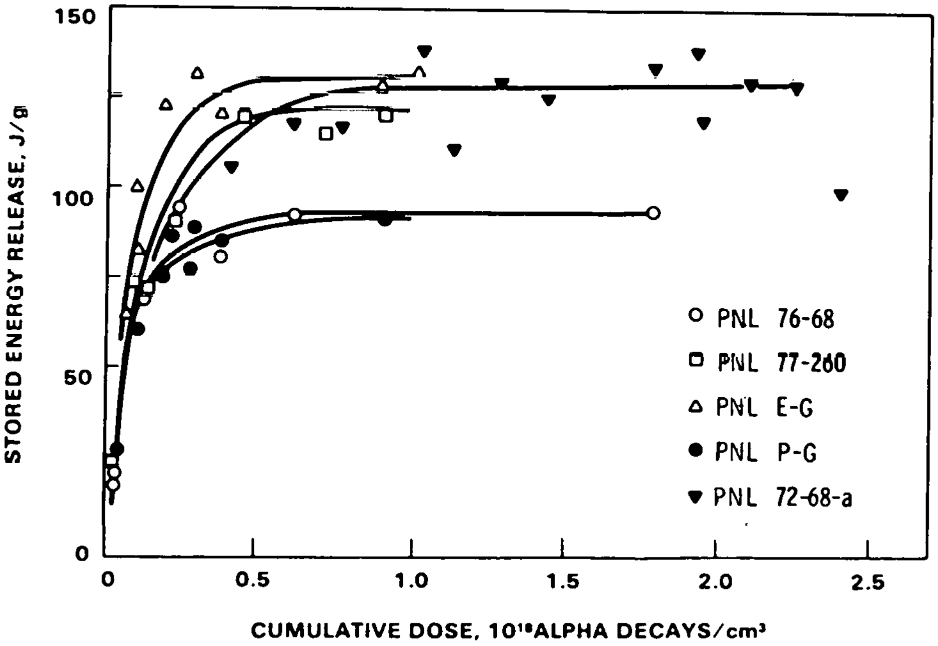

FIGURE 6.13. Stored Energy in ^{244}Cm-Doped HLW Glasses (Roberts, Turcotte and Weber 1981)

the crystalline phases (Weber et al. 1979). The recovery of the radiation-induced stored energy in the waste glasses of Figure 6.13 was investigated by 7-day isochronal anneals (Roberts 1980; Chick et al. 1980). The fractional recovery of these glasses at each annealing step is shown in Figure 6.14. The results show a single continuous recovery stage for all the waste-glass compositions which is complete at 360°C.

Several studies of stored energy in actinide-doped waste glasses have also been carried out abroad. At Harwell, Hall et al. (1976) measured stored energy release in a borosilicate waste-glass composition doped with 5 wt% $^{238}PuO_2$. The stored-energy release was measured by differential thermal analysis (DTA) at a constant heating rate of 1°C/min. The total energy release from specimens self-irradiated at 50°C for 1 year (2×10^{18} alpha decays/cm^3) was 97 J/g. The energy release from specimens self-irradiated at 170°C to the same dose was 82 J/g. This reduction in energy release at elevated storage temperatures supports the data in Figure 6.12. At the Nuclear Research Center in Karlsruhe (Scheffler, Riege and Hild 1976; Scheffler and Riege 1977) three

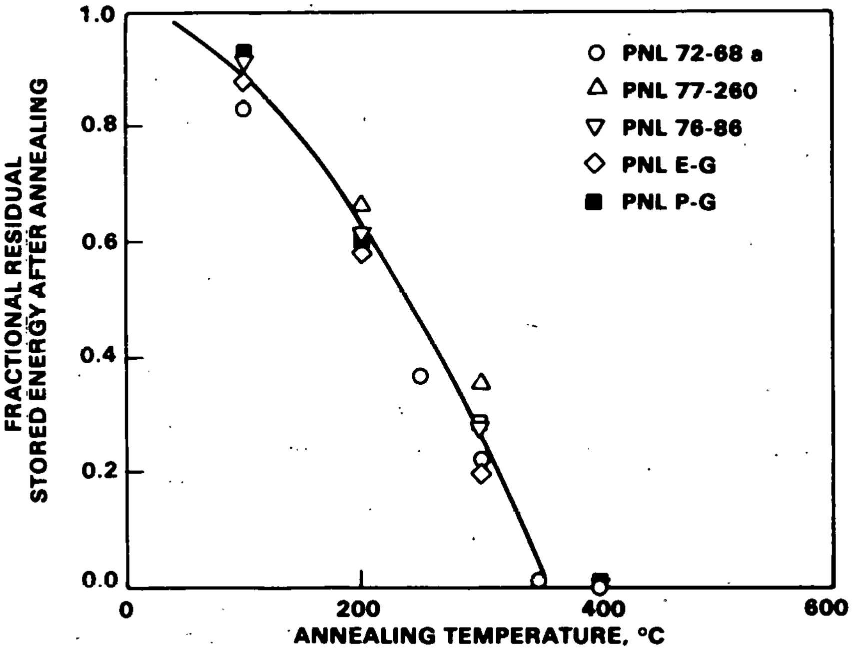

FIGURE 6.14. Thermal Recovery of Stored Energy in ^{244}Cm-Doped HLW Glasses (Roberts 1980)

HLW glasses were doped with ^{242}Cm and the stored energy measured as a function of dose out to ~6.6 x 10^{18} alpha decays/cm^3. The stored energy for the three waste glasses saturated at values ranging from 264 to 395 J/g after a dose of ~3 x 10^{18} alpha decays/cm^3. In the collaborative European Communities research program, Malow, Marples and Sombret (1980) measured the stored energy of four borosilicate glasses doped with $^{238}PuO_2$. The energy release was measured using a DSC on samples weighing ~30 mg at a constant heating rate of 2°C/min. The stored energies ranged from values of 43 to 78 J/g at a dose of 3.3 x 10^{18} alpha decays/cm^3.

All the currently available data on stored energy release in actinide doped waste glasses are summarized in Table 6.6. The results in Table 6.6 show that stored energy ranges from about 50 to 400 J/g, or 50 to 125 J/g if the data of Scheffler and Riege (1977) are excluded. Since the specific heat of the waste glasses is usually about 1 J/g • °C, the maximum temperature rise that could occur from the sudden release of the stored energy is 50 to 400°C,

TABLE 6.6. Summary of Stored Energy Measurements in Actinide-Doped Simulated HLW Glasses

Simulated HLW Glass	Storage Temp., °C	Maximum Dose, alpha decays/cm^3	Maximum Stored Energy, J/g	Reference
PNL 72-68-a	23	4.4 x 10^{18}	98	Roberts et al. 1976
PNL 72-68-b	23	30.0 x 10^{18}	121	Ross et al. 1978
PNL P-G	23	3.6 x 10^{18}	86	Ross et al. 1978
PNL E-G	23	3.6 x 10^{18}	125	Ross et al. 1978
PNL 76-68	23	3.6 x 10^{18}	83	Ross et al. 1978
PNL 77-260 (vitreous)	23	4.8 x 10^{18}	120	Weber et al. 1979
PNL 77-260 (700°C, 1 wk)	23	4.8 x 10^{18}	90	Weber et al. 1979
PNL 77-260 (6°C/hr)	23	4.8 x 10^{18}	86	Weber et al. 1979
UK 189	50	2 x 10^{18}	97	Hall et al. 1976
UK 189	170	2 x 10^{18}	82	Hall et al. 1976
Basic "98"	23	5.2 x 10^{18}	264	Scheffler and Riege 1977
HLW "98"	23	5.5 x 10^{18}	347	Scheffler and Riege 1977
HLW-GD "98"	23	6.1 x 10^{18}	395	Scheffler and Riege 1977
UK 189	23	3.3 x 10^{18}	78	Malow et al. 1980
UK 209	23	3.3 x 10^{18}	73.5	Malow et al. 1980
SON 68.30.20.U2	23	3.3 x 10^{18}	76	Malow et al. 1980
VG 98/3	23	3.3 x 10^{18}	55	Malow et al. 1980

or only 50 to 125°C if data of Scheffler and Riege (1977) are excluded. Temperature excursions of this magnitude should present no serious problems after several thousand years' storage, the amount of time required to reach these stored energy values.

6.2.3.2 Neutron Irradiation Data

Roberts, Jenks and Bopp (1976) measured the stored energy release in two borosilicate waste glass compositions irradiated at ~100°C with fast neutrons ($E > 1$ MeV) to two different fluence levels: 1.45×10^{20} n/cm^2 and 3.48×10^{20} n/cm^2. The results indicate that the stored energy has saturated at these fluences. The stored energies are ~98 J/g for one glass and ~88 J/g for the other glass (PNL 72-68). The neutron irradiation data for PNL 72-68 (~88 J/g) is in close agreement with the results shown in Table 6.6.

Antonini, Lanza and Manara (1979) measured stored energy in a borosilicate waste glass doped with ^{235}U and irradiated with fast neutrons to induce damage by the fissioning of the ^{235}U. The stored energy was measured with a differential scanning calorimeter at a constant heating rate of 10°C/min on samples irradiated to doses ranging from 1×10^{15} fissions/cm^3 to 4×10^{17} fissions/cm^3 (the upper dose is reported to correspond to 9.4×10^{18} alpha decays/cm^3). The maximum stored energy observed was ~82 J/g, which is in agreement with stored energy values measured in other actinide-doped waste glasses.

6.2.3.3 Charged-Particle Irradiation Data

Antonini et al. (1979; 1980) irradiated two borosilicate waste glasses and SiO_2 with 46.5 MeV Ni^{6+} ions to ~1 dpa (reportedly corresponds to ~2.6×10^{19} alpha decays/cm^3). The maximum stored energy for the two borosilicate glasses was ~165 J/g, whereas in the SiO_2 the maximum stored energy was ~210 J/g. These stored energy values are slightly higher than those observed from actinide decay, perhaps a result of the much higher displacement rates.

6.2.3.4 Gamma Irradiation Data

There have been no gamma irradiation experiments reported on glass waste forms that measured stored energy.

6.2.3.5 Transmutation Simulation Data

Stored energy is not being measured in the only currently reported transmutation study under way (Chick et al. 1980; Weber, Wald and Gray 1980).

6.2.4 Other Property Changes

The data available on other property changes (besides volume, leach rate, and stored energy) are very limited. For instance, no radiation-induced devitrification (crystallization) has ever been observed in HLW glasses; however, amorphization of crystalline phases has been observed in partially devitrified HLW glasses (Weber et al. 1979). This section reviews the remaining radiation effects data available on HLW glasses. These limited data cover mechanical strength/microcracking, helium buildup/release, and structural/ microstructural changes.

6.2.4.1 Mechanical Strength/Microcracking

Radiation can potentially affect the mechanical strength of a waste form by producing embrittlement or microcracking, which may lead to increased fracturing in the event of an accident during transportation and handling. Fracturing will produce fine particles that can be inhaled and also increases surface area; this can, in turn, increase the waste form's susceptibility to leaching.

Weber et al. (1979) performed impact tests on a vitreous and two partially devitrified forms of ^{244}Cm-doped PNL 77-260 waste glass. The results indicate that the impact performance was not adversely affected by the self-radiation; however, one of the partially devitrified forms of these glass compositions (containing large crystals from a slow cool at 6°C/hr) exhibited extensive microcracking associated with the amorphization of the crystalline devitrification product $[Ca_3Gd_7(SiO_4)_5(PO_4)O_2]$. No microcracking was observed in the other partially devitrified glass (smaller crystals from anneal at 700°C for 1 week), even though the same phase was present and also underwent amorphization. This same partially devitrified glass did, however, show microcracking after immersion in room temperature water for 3 weeks. Bibler and Kelley (1978) also observed microcracking in the actinide-doped HLW glasses they studied, but did not perform any mechanical strength tests. No other investigators have reported microcracking in irradiated HLW glasses.

Bonniaud et al. (1979; 1980) reported a slight decrease in the microhardness of actinide-doped HLW glasses as a result of radiation damage, and Scheffler and Riege (1977) reported that the mechanical properties of ^{242}Cm-doped HLW glasses were slightly altered after ~5 x 10^{18} alpha decays/cm^3.

6.2.4.2 Helium Buildup/Release

Helium, which results from the capture of two electrons by the alpha particles emitted in alpha decay, must either be accommodated interstitially, or diffuse to internal voids or the plenum of the canister. Helium buildup in waste forms can potentially produce embrittlement, swelling from bubble formation, or pressurization of the canister.

Turcotte (1976) made a detailed study of helium diffusion in ^{244}Cm-doped PNL 72-68. The diffusion of helium at short times and low fractional release values followed Arrhenius behavior; at longer times and higher fractional release values, the apparent diffusion coefficient is decreased by about one order of magnitude due to trapping effects at radiation-induced defects. The helium solubility was also measured and determined to be 1.5 x 10^{16} atoms/cm^3 at 400°C and 730 Torr helium. This leads to the conclusion that >99% of the helium generated in HLW glass will not remain in solution, but will diffuse to internal voids or pores, or to the canister plenum. There was insufficient experimental evidence to determine whether or not helium bubbles will form at ambient temperatures. In addition, helium pressurization of the canister containing waste from UO_2 fuel reprocessing was shown to be negligible, but canister pressurization may exceed 1 atmosphere if the sealed canisters contain waste from plutonium recycle fuel reprocessing.

Malow and Andresen (1979) investigated helium generation and diffusion in the same waste glass composition as Turcotte (1976); but instead of actinide doping, utilized the high ^{10}B (n, α) cross section by irradiating the waste glass (PNL 72-68) specimens in the thermal neutron flux of a reactor for 2 to 20 hr. At the maximum fluence (9.4 x 10^{18} n/cm^2), 1.5 x 10^{19} helium atoms/cm^3 were produced in the glass. The waste glass specimens were subsequently analyzed for fractional helium release at various temperatures. Evaluation of the results indicated that a nonideal diffusion process had occurred that was probably due to trapping of the helium at irradiation-induced defects. The apparent diffusion coefficient was found to decrease with dose, in agreement with the results of Turcotte (1976). The activation enthalpy increased with dose and saturated at a value of 110 kJ/mole at a dose of ~0.1 dpa (equivalent to ~2.5 x 10^{18} alpha decays/cm^3), which is approximately the dose where saturation of volume changes and stored energy are observed (see Sections 6.2.1 and 6.2.3). Scanning electron microscopy (SEM) revealed the apparent formation of helium bubbles at ~750°C, suggesting another possible helium transport mechanism that could delay helium release.

Malow, Marples and Sombret (1980) measured helium release in three borosilicate waste glasses and a phosphate waste glass, all doped with ^{238}Pu and stored at 170°C. Estimates of the diffusion coefficient (at 170°C) were also made for the three borosilicate waste glasses. They concluded that only a small fraction of the helium will be released from a glass monolith at lower temperatures (noting that most alpha decay events will occur after the glass has returned to ambient temperature). Similar results were obtained by Hall et al. (1976), who measured helium release in a ^{238}Pu-doped borosilicate waste glass. No helium release was measured in a specimen stored at 50°C. Measurable helium release was found in a specimen stored at 170°C and a diffusion coefficient and activation energy measured. Bonniaud, Jacquet-Francillon and Sombret (1980) measured helium release in ^{244}Cm, ^{241}Am and ^{238}Pu-doped waste glasses and observed higher fractional release in the ^{244}Cm-doped glass. No explanation for this observation or estimates of diffusion coefficients and activation energies were given. Scheffler and Riege (1977) also investigated helium release in ^{242}Cm-doped waste glass stored at room temperature to ~4.7 x 10^{18} alpha decays/cm^3, but observed no helium release within the detectability range of their equipment.

6.2.4.3 Structural/Microstructural Changes

Radiation-induced (or enhanced) structural changes (such as devitrification, phase separation, lattice expansions, crystal structure changes, and crystalline to amorphous transformations) and radiation-induced microstructural changes (such as the formation of bubbles, voids, and other extended defects and point defects) can affect volume, leach rate, stored energy, mechanical strength/microfracturing, and helium buildup/release. Although a fundamental understanding of these structural/microstructural effects could help to more confidently predict the long-term stability and chemical durability of HLW forms, little information is presently available.

Weber et al. (1979) investigated structural changes in ^{244}Cm-doped PNL 77-260 glass by x-ray diffraction techniques. Radiation-induced devitrification was not observed. In the two partially devitrified forms of this waste glass composition, the crystal phase, $Ca_3Gd_7(SiO_4)_5(PO_4)O_2$ with an apatite structure, transformed from a crystalline to an x-ray amorphous state as a result of concentrated alpha decay in this phase. Accurate lattice parameter measurements were not possible during this transformation. The amorphization of this crystal phase resulted in the microcracking (discussed above) observed in the glass specimens containing large crystals (slow cooled at 6°C/hr). The other major phase in both partially devitrified glasses, a Gd- titanate, was reported to be stable with respect to radiation damage. It has since been observed (unreported results of W. J. Weber at PNL) that this phase is unstable and does become x-ray amorphous at higher doses than covered in the initial work.

Kelley and Bibler (1978) observed the formation of blisters in ^{238}Pu-doped glass after exposure to the electron beam of a SEM and postulated that this effect may be due to helium agglomeration by electron beam heating. Dé et al. (1976) implanted 50 keV helium into a simulated borosilicate glass with an accelerator and observed bubble formation and surface blistering after heating the specimens to 600°C. They also observed this same behavior at room temperature when the helium was implanted through the ^{10}B (n, α) reaction by irradiating a glass-boron foil sandwich in a nuclear reactor. As noted above, Malow and Andresen (1979) observed helium bubble formation in neutron-irradiated PNL 72-68 after heating to 750°C.

Hall et al. (1976) observed no microscopic changes in a borosilicate waste glass irradiated at 300°C with 0.5 MeV electrons from a Van de Graaff accelerator; however, when the irradiations were carried out in a high-voltage electron microscope (HVEM), bubbles were observed to form at 200°C and above. The bubbles were postulated to contain oxygen.

6.3 RADIATION DAMAGE IN CERAMIC WASTE FORMS

As alternatives to glass waste forms, several ceramic waste forms have been proposed that are tailored to produce specific crystalline phases as hosts for radioactive waste products. Generally, fission products (such as cesium and strontium) are confined to one or more crystalline phases, and the actinides (uranium, neptunium, plutonium, americium, curium) to another set of phases. Three ceramic waste forms have received considerable attention: Supercalcine (McCarthy 1977), SYNROC (Ringwood et al. 1979), and glass ceramics (Dé et al. 1976). There has, however, been very little radiation damage work done to date on these or other ceramic waste forms. The data that are available are presented below.

6.3.1 Supercalcine (SPC-2)

The only radiation damage study that has been performed to date on one supercalcine formulation, SPC-2, was carried out at the Pacific Northwest Laboratory (PNL) and has been summarized by Rusin, Gray and Wald (1979). In that study the SPC-2 formulation was doped with 3 wt% Cm_2O_3 (2 wt% ^{244}Cm). X-ray diffraction, stored energy, and density measurements were made initially and at ~3-month intervals out to a total cumulative dose of ~7 x 10^{18} alpha decays/cm^3. Initial characterization of this supercalcine formulation showed it to consist of three major phases: fluorite, apatite, and a tetragonal phase. Subsequent analysis suggested that the curium predominantly entered the apatite and tetragonal phases.

X-ray diffraction analysis of the curium-doped supercalcine as a function of dose showed a gradual transformation of the apatite phase from a crystalline to amorphous state. An expansion in the unit cell of this phase was also observed with increasing dose. There was a slight increase in the intensity of the reflections associated with the tetragonal phase, but changes in the tetragonal unit cell were indeterminable. The fluorite peak was used as a standard, since this phase did not appear to accept the curium dopant and was unaffected by external radiation.

Stored energy and density measurements were also made as a function of dose for the curium-doped supercalcine. The stored energy reached a maximum value of about 42 J/g at a dose of ~2 x 10^{18} alpha decays/cm^3

and then decreased slightly with further increases in dose. The data indicate that energy release is not complete at 600°C (the upper limit of the calorimeter used); therefore, additional energy release may occur at higher temperatures (>600°C). The density decreased exponentially with dose from ~4.185 g/cm^3 to 4.120 g/cm^3 at 7 x 10^{18} alpha decays/cm^3 (Rusin, Gray and Wald 1979). Roberts at PNL reports density measurements out to ~26 x 10^{18} alpha decays/cm^3 with little additional change. The density change as a function of dose in SPC-2 is shown in Figure 6.15. The volume expansion at saturation (~1.5%) is partially attributed to the unit cell expansion observed in the apatite phase.

No leach testing of the ^{244}Cm-doped supercalcine formulation was performed. Rusin (1980), however, has suggested that leach rate changes in the supercalcine may be minimal since radiation damage effects are observed for

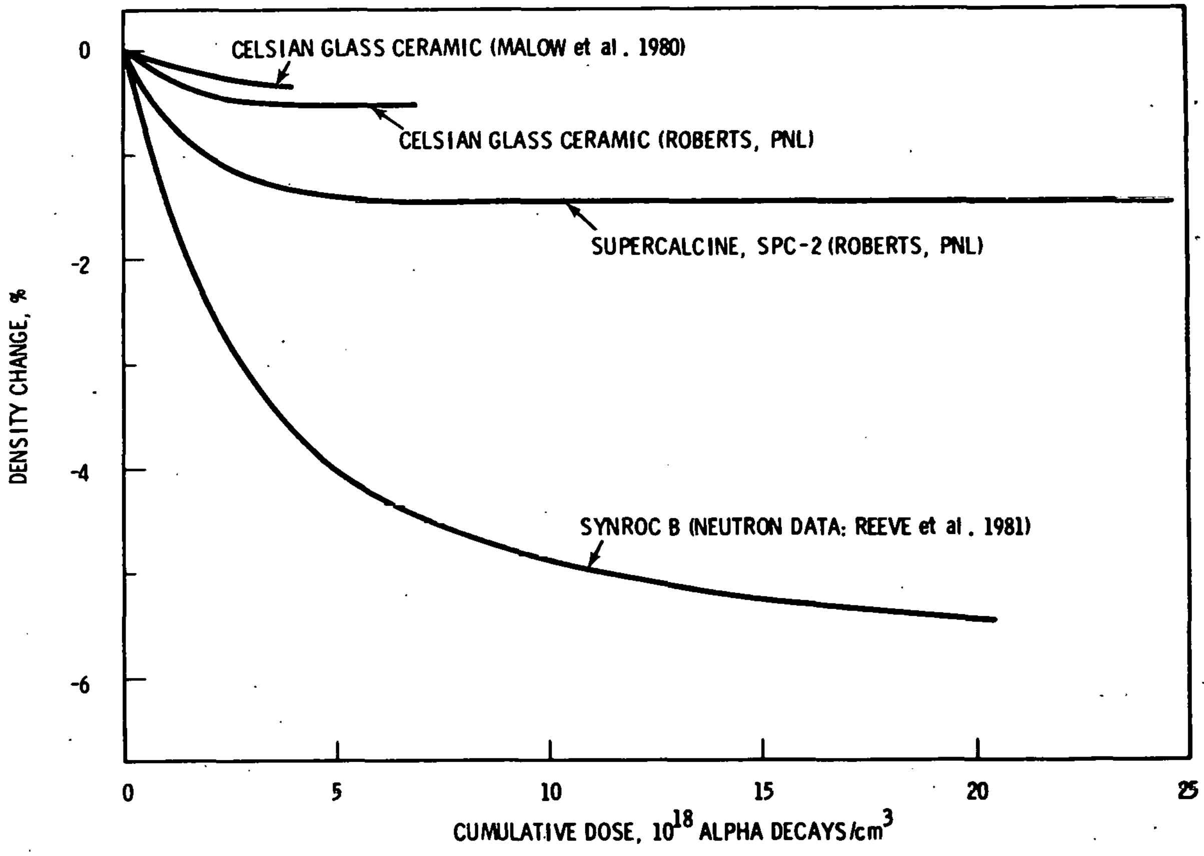

FIGURE 6.15. Density Changes in Ceramic Waste Forms

the apatite phase only and Weber et al. (1979) have shown that amorphization of a similar apatite phase does not significantly affect leach rates.

The effects of Cs → Ba transmutation in this same supercalcine formulation (SPC-2), but undoped, and in pollucite, the cesium host phase in SPC-2, are currently being investigated by Gray of PNL (Chick et al. 1980). Initial results (Weber, Wald, and Gray 1980) show no significant changes in density or leach rate. This study is continuing, and future data should establish whether these trends continue.

6.3.2 SYNROC

Ringwood, Oversby and Sinclair (1980) have argued that SYNROC is stable with respect to alpha decay damage, based on an assessment of natural minerals of uranium- and/or thorium-bearing perovskite and zirconolite, which are the actinide host phases of SYNROC. As stated earlier in this report (Section 6.1.3), such data can provide only qualitative results, and since zirconolite is observed to become metamict, the rate of metamictization (amorphization) or any other radiation damage effect may change with slight modifications in chemistry. Therefore, quantitative evaluation of SYNROC as a waste form requires radiation-damage testing of actual or simulated waste forms.

A limited amount of accelerated irradiation damage testing has been performed on SYNROC and its constituent phases by Reeve et al. (1980, 1981) using fast neutrons. Specimens of SYNROC B, SYNROC C, and their constituent minerals hollandite, perovskite and zirconolite were irradiated in the fast-neutron flux of the HIFAR reactor at Lucas Heights, for different lengths of time. The longest irradiation to date on the SYNROC specimens has been 13.4 x 10^{19} n/cm^2 ($E > 1$ MeV), which reportedly represents an equivalent SYNROC storage time of 1.2 x 10^5 years and corresponds to 0.36 dpa or ~20.5 x 10^{18} alpha decays/cm^3. Measurements of volume, density, open-porosity and lattice parameter changes were made. The volume expansion of SYNROC B is greater than that of perovskite, which in turn is greater than that of hollandite. The results, also illustrated in Figure 6.15 (neutron dose has been converted to an equivalent alpha decay dose), indicate that the volume expansion of SYNROC B will saturate at ~6.5%. Initial data at only a single dose for zirconolite and SYNROC C suggest that the volume expansion for zirconolite falls between perovskite and hollandite and that the volume of SYNROC C may expand slightly more than SYNROC B.

No leach testing has been performed on these irradiated specimens.

6.3.3 Celsian Glass Ceramic

A glass ceramic is the ceramic product derived from a homogeneous glass by annealing the glass at the temperature of maximum nucleation rate, followed by a high-temperature anneal to yield maximum growth rate. Through proper choice of the glass composition, crystalline phases may be tailored into the glass-ceramic product that are resistant host phases for the long-lived radionuclides (Dé et al. 1976). The celsian glass ceramic, developed at the Hahn-Meitner Institut (Berlin) and named for the predominant crystalline phase, is easy to fabricate, is homogeneously crystallized, and contains a variety of chemically resistant host phases for the radionuclides. Celsian glass ceramic as a waste form has been studied for potential radiation effects both at PNL (Ross et al. 1979; Weber, Wald and Gray 1980), in cooperation with the Hahn Meitner Institut, and as part of a collaborative research program within the European Community (Malow, Marples and Sombret 1980).

R. P. Turcotte and coworkers at PNL and W. Lutze of Hahn-Meitner Institut recently studied the effects of radiation damage in ^{244}Cm-doped celsian glass ceramic. As shown in Figure 6.15, density was observed to decrease exponentially with dose, saturating at a dose of ~3 x 10^{18} alpha decays/cm^3 (Roberts, Turcotte and Weber 1981). Volume expansion at saturation is about 0.5%. Stored energy also increased exponentially with dose to a value of ~80 J/g (saturation also occurred at ~3 x 10^{18} alpha decays/cm^3). X-ray diffraction data revealed that a curium-rich, rare-earth titanate phase in this waste form underwent a small volume expansion with dose and eventually became amorphous at the same saturation dose of ~3 x 10^{18} alpha decays/cm^3 (equivalent to ~5 x 10^{19} alpha decays/cm^3 in the rare-earth titanate phase, if all the curium concentrated in this phase). No leach testing was performed on this material.

In the study of Malow, Marples and Sombret (1980), the celsian glass ceramic was doped with 2.5 wt% ^{238}Pu. The density changed exponentially with dose, as shown in Figure 6.15, and the results suggest saturation will occur at ~5 x 10^{18} alpha decays/cm^3 with a corresponding volume expansion of ~0.5%, in good agreement with the results of Turcotte and coworkers above. The stored energy was measured to be 43 ± 5 J/g after a dose of ~3.3 x 10^{18} alpha decays/cm^3. This is approximately the value reported by Turcotte and coworkers, but it is not known whether saturation has occurred in this material. Changes in leach rates were measured for specimens stored at 23 and 170°C to a cumulative dose of ~3.3 x 10^{18} alpha decays/cm^3. The leach rate decreased by ~19% in the specimen stored at 23°C, while the leach rate decreased by only ~4% in the specimen stored at 170°C. The fractional helium release was also determined to be ~3% after storage at 170°C to a cumulative dose of ~3.3 x 10^{18} alpha decays/cm^3.

6.3.4 Other Materials

There have been several studies reported of pure actinide compounds or actinide-doped phases that contribute to the understanding of radiation effects from alpha decay in nuclear waste solids. Much of this work has been recently reviewed by Weber and Turcotte (1980). Of particular importance is the data on self-damage from alpha decay in the actinide dioxides: PuO_2 (Chikalla and Turcotte 1973; Noe and Fuger 1974; Mendelssohn et al. 1967), AmO_2 (Mendelssohn et al. 1967; Hurtgen and Fuger 1977) and CmO_2 (Noe and Fuger 1971; Mosley 1971). All these compounds have the same fluorite structure as UO_2, which is a potential crystalline phase in some ceramic formulations proposed as waste forms. The most accurate available data from x-ray diffraction studies are summarized in Figure 6.16. The unit cell expansions all increase exponentially with dose and at saturation vary with the ionic radius of the constituent actinide, as would be expected. The important point is the relative constancy of the behavior over several orders of magnitude in the dose rates (proportional to the half-lives, which are ^{240}Pu 6580 years; ^{239}Pu 24,400 years; ^{238}Pu 87.7 years; ^{241}Am 458 years; and ^{244}Cm 18.1 years). No tendency toward amorphization is reported for any of the actinide dioxides.

Several single-crystal and polycrystalline materials have been irradiated at room temperature with alpha particles emitted from a thick $^{238}PuO_2$ source

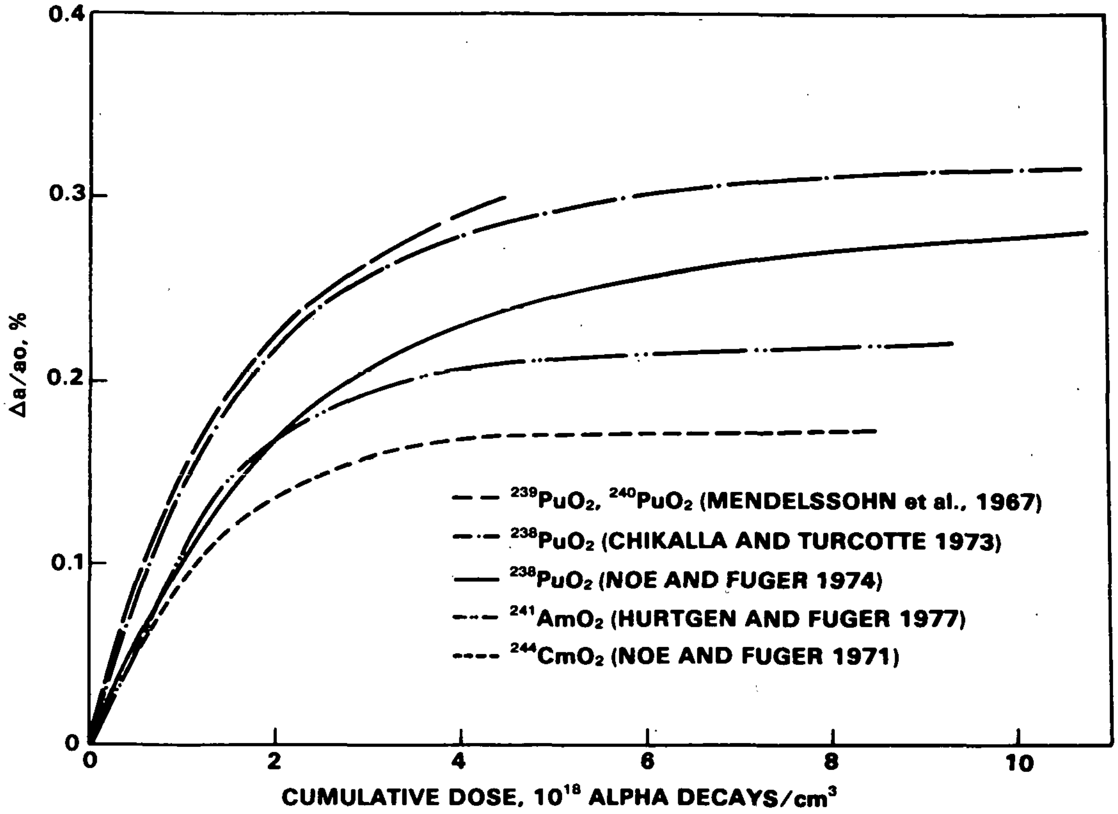

FIGURE 6.16. Lattice Expansions from Self-Radiation Damage in Several Actinide Dioxides

(E_{max} = 5.5 MeV) to simulate the alpha-particle flux incident on the nonactinide-containing phases in nuclear waste solids (Weber, Wald and Gray 1980; Weber and Turcotte 1980; Chick et al. 1980). The relative changes in lattice parameters, measured by x-ray diffraction techniques, as a function of alpha dose are shown in Figure 6.17. The observed damage ingrowth follows the same exponential relationship observed for alpha decay. The results indicate that nonactinide-containing phases may undergo significant lattice expansion as a result of alpha bombardment from adjacent actinide host phases.

Clinard and Hurley (1979) summarized studies of general radiation effects and their potential application to nuclear waste forms. At the long-term damage levels expected for ceramic waste forms (1 to 10 dpa), some materials show little effect while others undergo major structural changes. They concluded that there are several major material characteristics that seem to enhance irradiation stability: cubic crystal structure, high helium permeability,

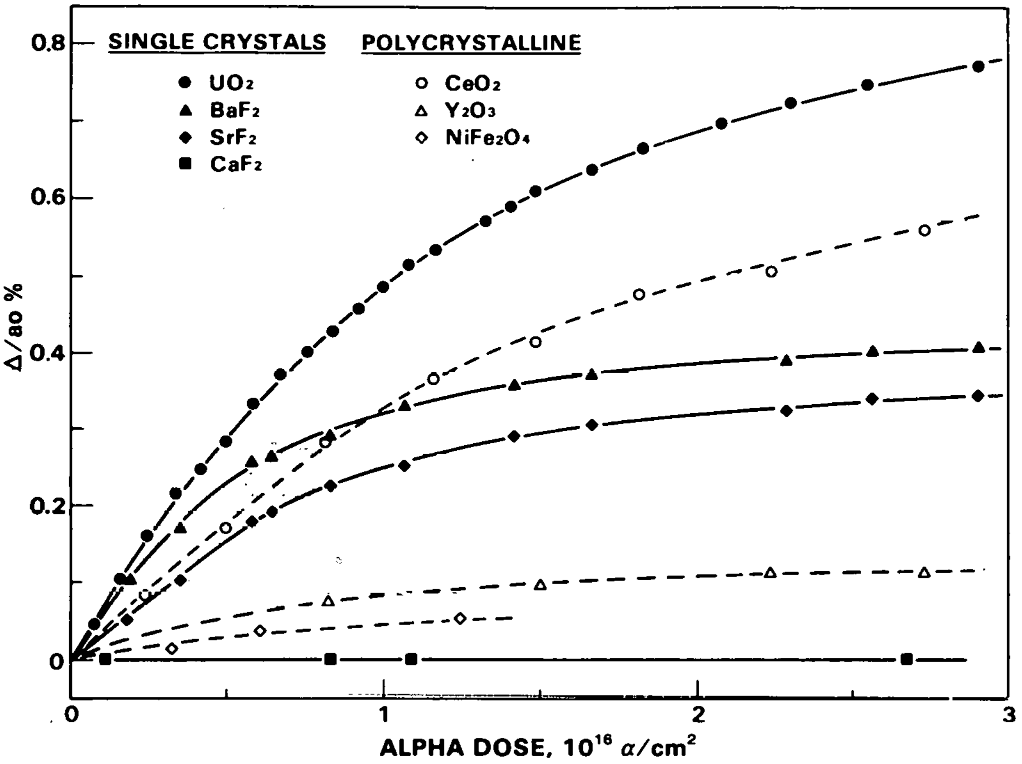

FIGURE 6.17. Lattice Expansions for Several Cubic Structures Irradiated with Alpha Particles Emitted from a $^{238}PuO_2$ Source (Weber and Turcotte 1980)

large internal surface area, high fracture toughness, high ionic bonding character, dense atomic packing, and low propensity for absorption of water. There are inevitable contradictions, but knowledge of these factors should help in the identifying of waste forms having high stability characteristics.

Naguib and Kelly (1975) examined several criteria that may be useful in predicting if a ceramic material will be subject to irradiation-induced amorphization. Using available data for energetic heavy-ion bombardment of 72 nonmetallic solids, they deduced both a temperature-ratio criterion and a bond-type (ionicity) criterion that successfully predict the occurrence of amorphization or crystallization. The temperature-ratio criterion, based on a physical model involving thermal spikes, predicts that amorphization should occur whenever the ratio, crystallization temperature/melting point, exceeds 0.3. The bond-type criterion states that amorphization should occur whenever the ionicity is ≤ 0.47.

Stored energy in ceramic waste forms may potentially reach higher values than observed in glass waste forms. Some irradiated crystalline materials are known to exhibit rather large energy releases when the radiation damage is thermally annealed. A notable example is neutron-irradiated graphite, which undergoes enthalpy changes greater than 2400 J/g (Woods, Bupp, and Fletcher 1956). Neutron-irradiated refractory oxides are more typical of the expected behavior of crystalline phases in ceramic waste forms. Stored energy values for several materials are shown in Table 6.7. The maximum observed values lie between 100 and 350 J/g.

Roberts, Jenks and Bopp (1976) measured stored energy in neutron-irradiated simulated PW-4m calcine, PW-4m calcine on alumina spheres, and a compact made by hot-pressing PW-4m calcine mixed with quartz sand. The compact gave a maximum stored energy value of 134 J/g, while the calcine and calcine on alumina stored energy values were substantially lower at 60 to 75 J/g.

Radiolysis from both gamma and alpha irradiation in concrete containing simulated Savannah River Plant waste was studied by Bibler (1978). With gamma radiolysis, hydrogen was the only significant product. With alpha radiolysis, hydrogen and oxygen were produced. Tingey and Felix (1977) also studied radiolysis from both gamma and alpha irradiation, but in a calcine (PW-7-2).

TABLE 6.7. Stored Energy in Several Neutron-Irradiated Ceramics

Material	Maximum Observed Stored Energy, J/g	Reference
SiO_2 (amorphous)	176	Roux et al. 1971
Al_2O_3	117	Roux et al. 1971
MgO	105	Roux 1969
BeO	334	Heur and Stolarski 1966
Steatite ($MgO \cdot SiO_2$)	250	Bopp and Towns 1964
Cordierite ($2\ MgO \cdot 2\ Al_2O_3 \cdot 5\ SiO_2$)	176	Bopp and Towns 1964

They reported that gas generation rates for both gamma and alpha radiolysis appeared to be about the same; however, there was a clear distinction in the gases generated. The gamma radiolysis yielded nearly 100% O_2, while a wide range of products were observed from alpha radiolysis.

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7.0 THERMAL PHASE STABILITY

R. P. May and R. P. Turcotte

The assessment of nuclear waste solids has often included studies of the effects of thermal treatment on waste form properties. One need is to evaluate the self-heating of wastes due to radioactive decay of certain isotopes, especially cesium and strontium. Moreover, geometrically large products have been planned: for example, canisters of waste glass 0.5 m in diameter and 3 m tall have been produced in development studies. As a result, depending on the glass composition, some devitrification may occur during slow cooling from the preparation temperature. In phosphate glasses, favored in early waste glass development work, significant decreases in chemical durability occurred as a result of partial crystallization. Highly radioactive waste from unaged fuel reprocessing could also lead to high waste-form centerline temperatures. For these reasons, thermal stability studies were included in development of borosilicate glasses and in part have led to development of more thermally stable glass-ceramic and crystalline forms. Centerline temperatures for waste forms can be controlled by adjusting radionuclide content. Studies summarized here, nonetheless, show relatively small effects from post-preparation thermal treatment for currently favored glass and ceramic compositions over a wide range of potential or accelerated treatments.

The present review includes most of the relevant thermal stability work on waste forms under anhydrous conditions but excludes volatility losses (described in Section 5). The major categories of proposed waste forms are addressed, though little information is available in some cases. The review for each type of material considers 1) what phase changes occur as a function of time, temperature, etc., and 2) what impact do these changes have on subsequent properties. Details of experimental approaches used by investigators are not germane to the review. Likewise, tables of some waste form compositions are given but are generally referenced. Glasses and crystalline forms are considered separately in the following sections.

7.1 GLASS FORMS

Glasses are well known to be in a metastable condition and to crystallize at rates depending on various parameters, the most important of which are the glass composition and temperature. Studies of simple glasses, often ternary oxides, have led to a "theory of crystallization" (e.g., see Kingery et al. 1976, Chapter 8 and references therein) based mainly on the estimated free-energy difference between the glass and its crystalline form, the glass viscosity and the diffusion coefficient(s) involved. Although the theory available assumes the simplest case--a crystalline phase grows in a glass of the same composition, application to waste glasses has been attempted by Boulos et al. (1980). They conclude that waste glasses will not significantly crystallize at 450°C until 10^4 years nor until 10^{35} years at ambient temperatures. Although these seem to be highly optimistic extrapolations, there is clearly a need for theoretical work. The experimental studies so far undertaken, especially by Turcotte and coworkers (1976-1981), show surprisingly regular behavior, considering the complexity of the glasses. These studies show that kinetic behavior can be defined in reasonable detail and that behavior agrees with general expectations based on theory.

Historically, the development of solid waste forms evolved through chemistry/chemical engineering needs, with increasing involvement by materials scientists. Early work emphasized phosphate glasses for engineering reasons, but interest in them decreased in favor of borosilicates in part because of devitrification problems (Mendel 1972; Grover 1973; Heimerl 1975). The Pamela metal-matrix concept, however, initially involved phosphate glass beads (Heimerl 1979), but poor hydrothermal leaching behavior (Marples et al. 1980) has probably ended consideration of phosphate glass as a HLW form. This change in direction occurred, however, without any study actually describing the kinetics of phosphate glass devitrification (Malow et al. 1980).

Before 1975, glass thermal stability studies were limited to a cursory evaluation of the tendency to devitrify, with an emphasis on the resultant change in chemical leachability. Although many laboratories evaluated thermal stability of waste glasses in some fashion, very few studies showed quantitative time- or temperature-dependent behavior. As work on borosilicate glasses continued, some kinetic studies were undertaken, particularly at PNL. The following sections attempt to summarize observed phase changes, the kinetics of some of these changes, and finally the practical significance of the changes, particularly with respect to leach rate.

7.1.1 Observed Phases

A large variety of glasses have been studied for waste immobilization, and some of the more thoroughly studied compositions are listed in abbreviated form in Table 7.1. As-prepared glasses may contain several percent of crystalline phases (e.g., RuO_2, Pd), and the borosilicates are probably phase-separated into boron-rich and boron-depleted vitreous regions at the ~100 Å level, as shown by Tomozawa et al. (1979). Liquid-liquid immiscibility also occurs on the macroscopic scale as demonstrated by the "yellow phase" reported for glasses containing more than a few percent of molybdate (Lutze et al., 1979). This molybdate phase may form during processing, is water-soluble, and concentrates both strontium and cesium.

Table 7.2 summarizes the crystalline phases formed in waste glasses after various heat treatments. There are some common features in phase study work difficult to convey in this tabular form. First, in all studies incorporating the platinum group metals, palladium, rhodium, and ruthenium (as RuO_2) are always found as discrete phases imbedded in the glass matrix, even in glasses quenched from the preparation temperature. Secondly, refractory oxides, such as $(Ce,RE^{3+})O_{2-x}$ or $(Fe,Cr,Ni)_3O_4$, may form rapidly at high temperatures and may also appear in quenched glasses or appear with later heat treatment. In PNL studies, more complex silicate, phosphate and aluminum or titanium containing phases generally form at lower temperatures, requiring relatively long heat treatments. Thermal treatment of up to 1 year at temperatures below the dilatometric softening point causes no measurable increase in crystallinity (Turcotte et al. 1980). The kinetic behavior follows theoretical expectations in that the refractory oxides have a larger driving force (ΔG) for formation than do silicates, phosphates, etc. Hence they crystallize rapidly, with higher liquidous temperatures.

TABLE 7.1. Nuclear Waste Glass Compositions, wt%

	SON 58.30.20.U2	VG 98/3	UK 209	UK 189	B 1-3	P 78/7	G 2	PNL 72-68	PNL 76-68	PNL 77-107	PNL 77-260	PNL 73-157	SRL C-411	SRL T-411	SRL T-211	ICPP Zr-13	ICPP Zr-51
SiO_2	43.6	41.8	50.9	41.5	18.0	--	43.9	27.3	39.8	37.8	35.8	41.6	43.3	42.8	43.7	34.8	44.4
B_2O_3	19.0	10.5	11.1	21.9	6.4	--	14.3	11.1	9.5	12.9	9.0	14.4	8.3	7.9	7.8	9.0	5.5
Al_2O_3	0.1	1.2	5.1	5.0	12.8	4.9	4.1	--	--	--	2.0	3.6	11.7	3.7	3.6	6.0	6.0
P_2O_5	0.6	--	0.2	0.2	--	48.5	--	--	--	--	2.4	--	--	--	--	--	--
CaO	--	2.3	--	--	4.0	--	2.0	1.5	2.0	2.0	1.0	3.2	5.0	5.4	5.2	3.1	1.2
BaO	1.0	0.6	0.4	0.4	15.5	1.5	0.6	2.5	0.6	1.1	0.6	3.6	--	--	--	--	--
Na_2O	9.4	22.3	8.3	7.7	3.8	--	10.0	4.1	12.5	5.4	11.1	8.6	9.4	9.0	15.1	19.0	16.1
Li_2O	--	--	4.0	3.7	2.4	--	3.1	--	--	--	--	2.0	9.4	8.8	3.1	1.4	--
Fe_2O_3	0.6	0.7	2.7	2.7	1.5	15.7	6.8	1.0	9.8	0.9	1.2	1.8	8.0	15.1	15.2	--	--
MoO_3	3.3	2.2	1.8	1.8	2.4	4.2	1.6	4.0	2.3	4.3	2.0	1.6	--	--	--	--	--
NiO	0.1	0.2	0.4	0.4	0.2	0.2	0.5	0.7	0.2	0.1	--	0.1	0.6	1.9	1.9	--	--
ZnO	--	--	0.4	0.4	3.6	--	2.0	21.3	5.0	5.0	--	2.5	--	--	--	1.4	--
ZrO_2	3.1	2.4	1.4	1.4	3.4	4.0	1.6	3.1	1.8	3.2	1.5	5.3	--	--	--	6.8	6.8
PdO	1.0	0.6	0.4	0.4	0.1	1.3	0.4	0.9	0.5	1.2	0.5	--	--	--	--	--	--
Cs_2O	1.8	1.4	0.8	0.8	1.8	2.1	1.4	1.8	1.1	1.9	0.8	1.0	--	--	--	--	--
RuO_2	1.9	1.1	0.7	0.7	--	2.3	0.9	1.9	1.1	2.2	0.9	--	--	--	--	--	--
SrO	0.7	0.5	0.3	0.3	0.6	0.8	0.6	2.1	--	--	--	--	--	--	--	--	--
U_3O_8	3.6	1.2	0.1	0.1	0.5	2.4	0.5	1.3	4.6	3.7	5.7	--	--	--	--	--	--
Rare earth oxides	7.7	5.5	3.7	3.6	5.1	9.8	4.3	7.7	4.4	8.6	14.0	5.3	--	--	--	--	--
Others[a] as $\frac{wt\%}{oxide}$			$\frac{6.3}{MgO}$	$\frac{6.3}{MgO}$	$\frac{1.2}{MgO}$	$\frac{0.5}{MnO_2}$	$\frac{2.0}{K_2O}$	$\frac{4.1}{K_2O}$		$\frac{4.0}{K_2O}$	$\frac{2.0}{K_2O}$	$\frac{3.2}{K_2O}$	$\frac{2.6}{MnO_2}$	$\frac{4.0}{MnO_2}$	$\frac{4.0}{MnO_2}$	$\frac{18.5}{CaF_2}$	$\frac{18.5}{CaF_2}$
	$\frac{0.7}{Tc_2O_3}$	$\frac{3.5}{TiO_2}$			$\frac{4.6}{TiO_2}$	$\frac{0.5}{Y_2O_3}$			$\frac{3.0}{TiO_2}$	$\frac{3.0}{TiO_2}$	$\frac{6.0}{TiO_2}$						
	$\frac{0.5}{TeO_2}$		$\frac{0.6}{Cr_2O_3}$	$\frac{0.6}{Cr_2O_3}$	$\frac{0.5}{Cr_2O_3}$	$\frac{0.6}{TeO_2}$					$\frac{3.0}{CuO}$						$\frac{1.3}{CuO}$

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[a] Other oxides are listed only if present >0.5 wt%.

TABLE 7.2. Crystalline Phases Identified in Nuclear Waste Glasses

Glass / Phase	SON$^{(a)}$ 58.30.20	Vg$^{(a)}$ 98/3	UK$^{(a)}$ 209	UK$^{(a)}$ 189	B$^{(a)}$ 1/3	P$^{(a)}$ 78/7	G$^{(b)}$ 2	PNL$^{(c)}$ 72-68	PNL$^{(c)}$ 76-68	PNL$^{(d)}$ 77-107	PNL$^{(c)}$ 77-260	PNL$^{(c)}$ 78-157	SRL$^{(c)}$ C-411	SRL$^{(e)}$ T-411	SRL$^{(c)}$ T-211	ICPP$^{(f)}$ Zr-13	ICPP$^{(f)}$ Zr-51
Ru				X													
Pd		X		X		X		X	X	X	X						
RuO_2	X	X	X	X		X		X	X	X	X						
PdO	X			X													
CeO_2	X	X	X	X		X	X	X	X	X	X	X					
$(Re)_2O_3$	X		X			X											
$(RE)PO_4$	X		X	X		X											
$(RE)_2SiO_5$				X			X										
$(RE)_2Ti_2O_7$					X						X						
$(RE)MoO_6$		X	X														
$(RE)BO_3$		X															
$(RE)_2TeO_5$	X	X															
PdTe	X					X											
Pd_3Te	X	X				X											
UTe						X											
$CdTeO_3$	X																
$FeCr_2O_4$				X													
$(Fe,Mg)(Cr,Fe)_2O_4$				X													
$(Ni,Mn)Fe_2O_4$								X	X	X	X		X	X	X		
ZrO_2																X	X
CaF_2																X	X
SiO_2	X	X															
$MgSiO_3$			X														

TABLE 7.2 (contd)

Glass / Phase	SON(a) 58.30.20	VG(a) 98/3	UK(a) 209	UK(a) 189	B(a) 1/3	F(a) 78/7	G(b) 2	PNL(c) 72-68	PNL(c) 76-68	PNL(d) 77-107	PNL(c) 77-260	PNL(c) 78-157	SRL(c) C-411	SRL(e) T-411	SRL(c) T-211	ICPP(f) Zr-13	ICPP(f) Zr-51
Na(Mg,Fe,Ni)Si_2O_6			X						X					X	X		
Li_2SiO_3													X	X			
$NaAlSiO_4$													X	X	X	X	X
(Cs,Na)$AlSi_2O_6$					X												
$BaAl_2Si_2O_8$					X												
Zn_2SiO_4								X									
$CaZrSi_2O_9$																X	X
$NaAlMoO_4(SiO_4)_6$					X												
(Ca,Ba,Sr)MoO_4	X		X		X		X	X		X							
$Ca_3Gd_7(SiO_4)_5(PO_4)O_2$											X						
(Al,Fe)(PO_4)						X											
$Zr_2P_2O_7$						X											

(a) Malow et al. 1980
(b) Araki 1981
(c) Turcotte et al. 1980
(d) Wald and Westsik 1979
(e) Chick et al. 1980
(f) Lukacs et al. 1978

7.1.2 Composition Effects

A wide range of waste-glass compositions have been examined in response to the wide variations in proposed or actual waste-stream compositions that must be vitrified. In addition, composition variations within individual waste storage tanks are large, suggesting that waste-form properties should be examined over a range of compositions as undertaken, for example, in Savannah River Laboratory (SRL) studies (Kelley 1975). In the only detailed study reported, Chick et al. (1979; 1980) evaluated waste glasses formed from 11 representative oxides (Table 7.3) covering the range of then-proposed compositions in the United States. Figure 7.1 shows the rather broad range of compositions involved, considering the glasses as composed of network formers,

TABLE 7.3. Composition Field for Eleven-Compound Generic Study

Component	Low Value, mole%[a]	High Value, mole%[a]	Centroid Value, mole%
Formers			
SiO_2	42	58	49.03
B_2O_3	6	12	8.82
Al_2O_3	0	15	7.35
Modifiers			
CaO	0	14	6.86
MgO	0	8	3.92
Na_2O	11	16	13.24
Intermediates			
ZnO	0	6	2.94
TiO_2	0	3	1.47
Cr_2O_3	0	3	1.47
Fe_2O_3	0	3	1.47
NiO	0	3	1.47

(a) The field was also limited by these restrictions: total formers 55-75 mole%; total modifiers 14-34 mole%; total intermediates 0-22 mole%.

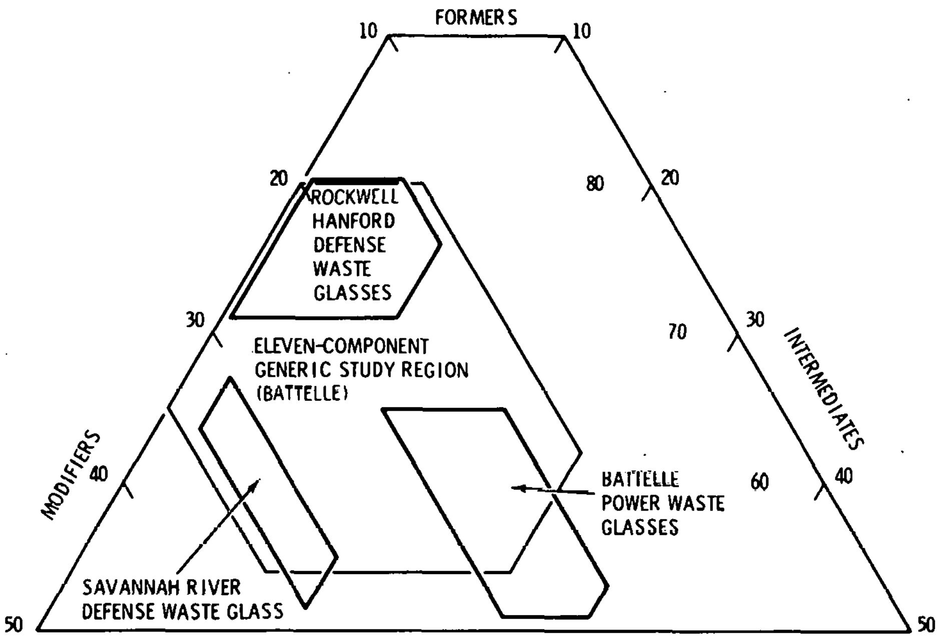


FIGURE 7.1. Ternary Diagram of Glass Formers, Modifiers and Intermediates, Showing Nuclear Waste Glass Composition Regions and Experimental Fields (from Chick 1980)

modifiers, and intermediates as defined in Table 7.3. Empirical modeling of data from this matrix allowed correlations between composition and a number of physical and chemical properties.

One parameter studied was the devitrification yield following heat treatment. The crystalline yields were determined by x-ray diffraction in both quenched and slow-cooled (6°C/hr) samples. Correlations with individual oxide concentrations are shown in Figure 7.2a and b. The insoluble phase concentrations in quenched glasses increased with increasing concentrations of transition metals and titanium and decreased with Na_2O, CaO, and SiO_2 additions. In the slow-cooling experiments, SiO_2 and B_2O_3 concentrations are of primary importance in reducing crystalline yields. The positive influence of Al_2O_3 in increasing devitrification is supported in studies by Plodinec and Wiley (1979). The inhibitory effect of MgO additions on devitrification has been reported in other glass studies (e.g., Nikiforov et al. 1979; Shahid and Glassner 1972).

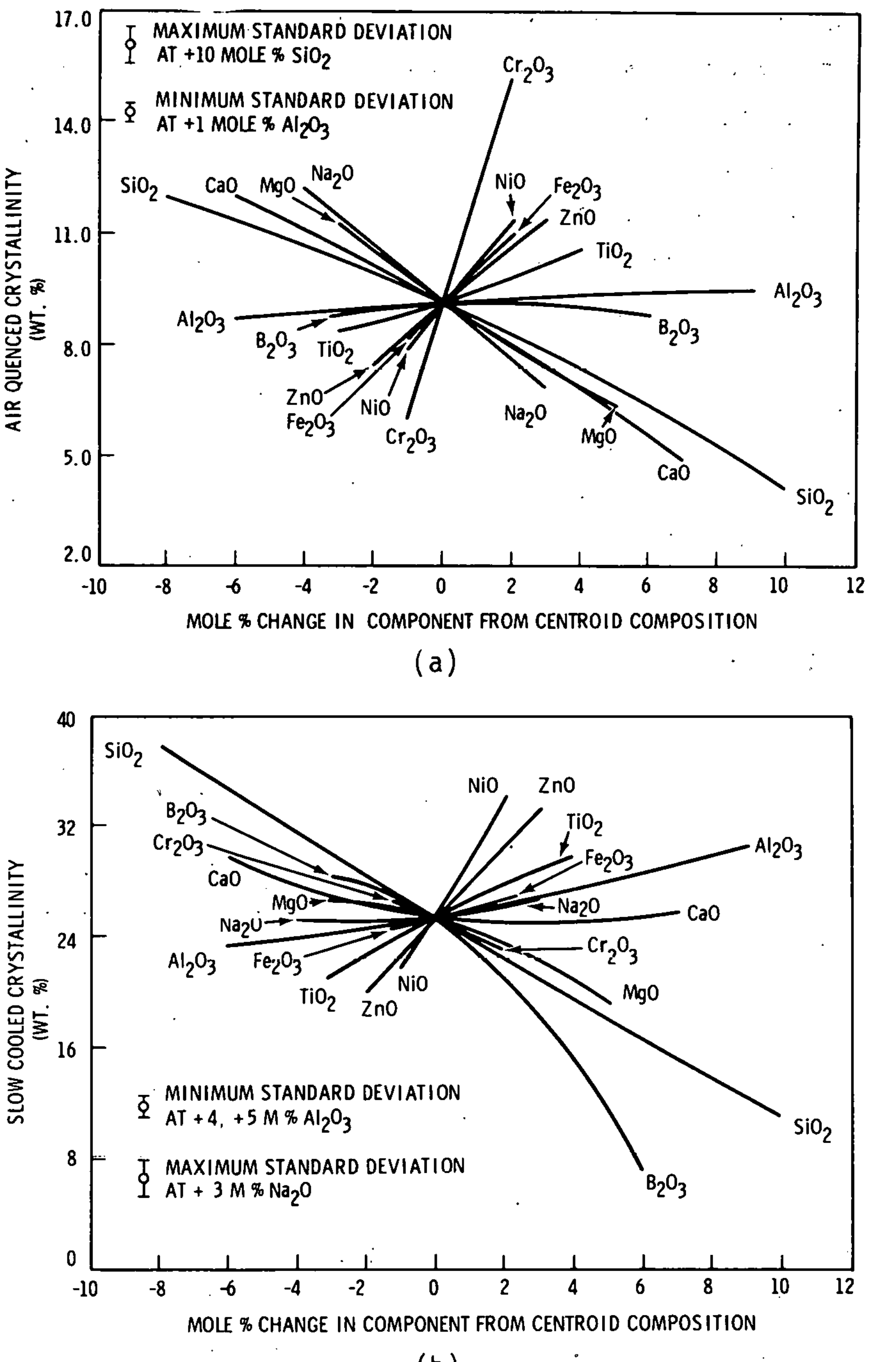
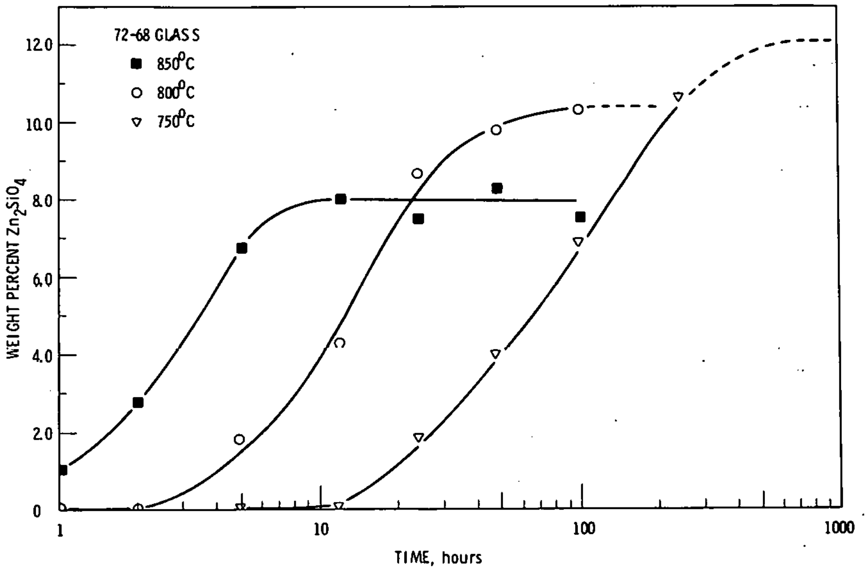


FIGURE 7.2. Effects of Glass Composition Component Changes from Glass Centroid Composition on Crystallinity After a) Rapid Air Cool (Quench) and b) Slow Cool at 6°C/hr from the Melt (from Chick 1980)

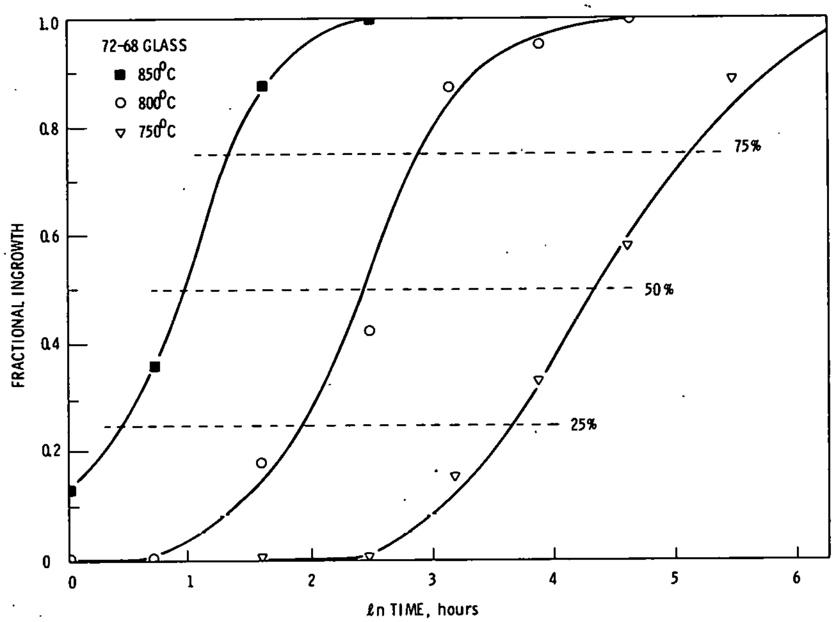
Spinel formation has received special attention because of settling problems in ceramic melters. Mellinger and Chick (1979) and Mellinger et al. (1980) showed that increasing the concentrations of either Fe_2O_3 or Al_2O_3 increased the formation of $(Mn,Ni)Fe_2O_4$. The aluminum atoms apparently preferentially occupy sites that iron, nickel, or manganese usually occupy in the glass structure. This results in the exclusion of these metals from the glass network and forces spinel formation when aluminum is above a minimum concentration (>10 mole%) in the glass (MacKenzie and Brown 1975). Another study (Chick 1980) has shown that Li_2O substitution for Na_2O also increases spinel yield as was observed in a study of three SRL glasses (C-411, T-411, T-211). Further work (May 1980) demonstrated important viscosity correlations (involving Li_2O concentration) on both crystalline yield and microstructure of the heat-treated glasses.

7.1.3 Kinetic Studies

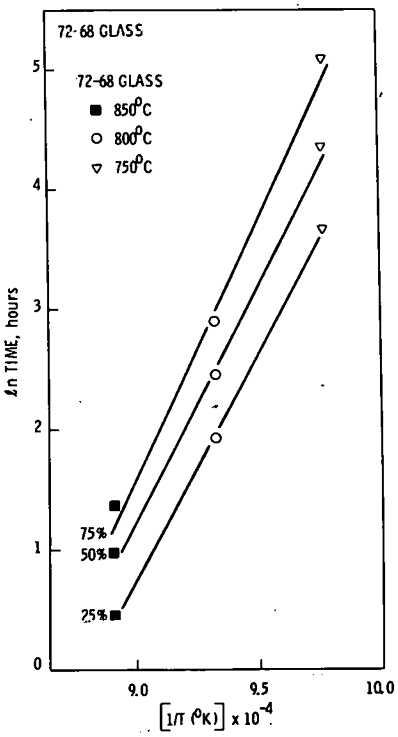
In the first detailed study of waste-glass devitrification, Turcotte and Wald (1978) reported time- and temperature-dependent results for glass 72-68, a zinc borosilicate composition. Figure 7.3a, b, c summarizes the information generated for ingrowth of Zn_2SiO_4, which was the major devitrification product. Regular, sigmoidal ingrowth curves and a good 1/T rate dependence were observed. Turcotte, Wald, and May (1980) later refined these data and similar information for glass 76-68 into time-temperature-transformation (TTT) curves as shown in Figure 7.4. Results are also shown for PNL 77-260, and a partial curve is included from results given by Malow et al. (1980) on glass UK-189. The latter work relied on microscopic examination rather than the x-ray diffraction method used in PNL studies. All curves (Figure 7.4) show the minimum heat treatments necessary to cause 5 wt% crystalline ingrowth beyond the 2 to 5% melt-insoluble crystalline content that is present before heat treatment. Most of the data available for other glass compositions fall near or within the region defined by these curves. The relatively narrow band observed is probably a result of a glass-development criterion that viscosity should be 200 poise or less at 1050°C. Hence, most waste-glass compositions studied have similar ion mobilities in the melt.



(a) Weight % Ingrowth of Zn_2SiO_4 as a Function of Time at 750, 800 and 850°C



(b) Fractional Ingrowth of Zn_2SiO_4 Versus ln Time for Isothermal Anneals at 750, 800 and 850°C



(c) Natural Log Time Versus Inverse Temperature for 25, 50 and 75% Ingrowth of Zn_2SiO_4 at Anneal Temperatures of 750, 800 and 850°C

FIGURE 7.3. Crystalline Ingrowth of Zn_2SiO_4 in Glass PNL 72-68 as a Function of a) Time, b) ln Time and c) Inverse Temperature for Isothermal Anneals at 750, 800 and 850°C (from Turcotte et al. 1980)

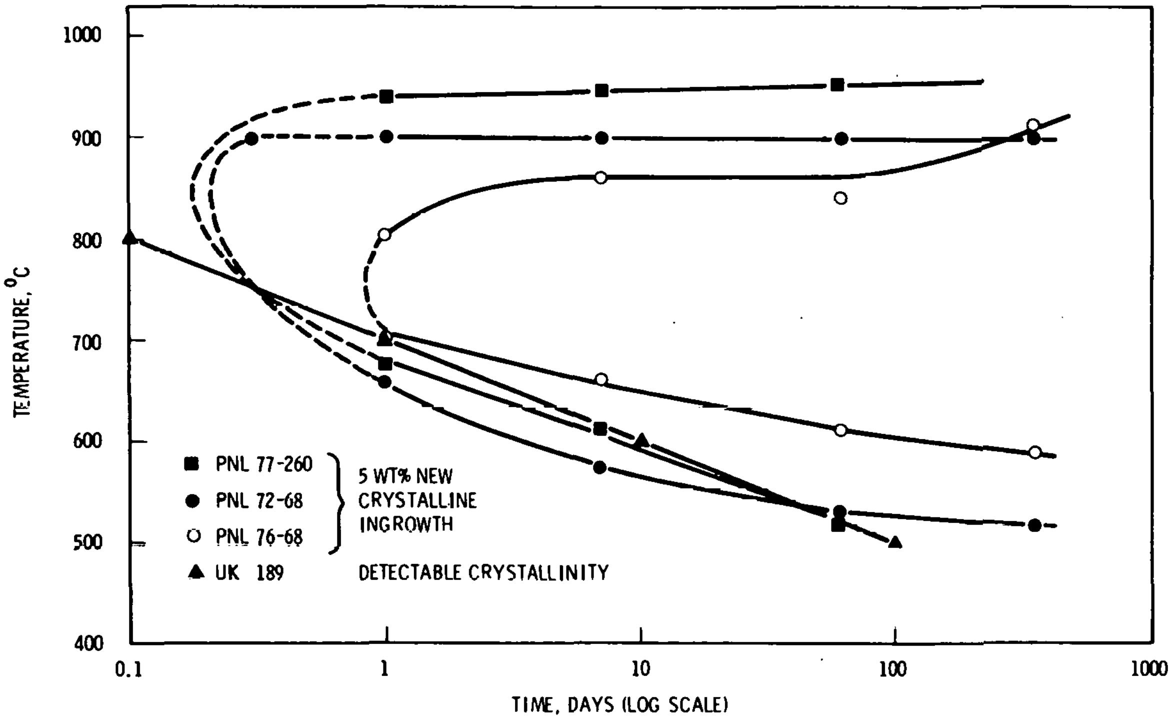


FIGURE 7.4. Time-Temperature-Transformation (TTT) Curves for Glasses PNL 72-68, 76-68 and 77-260 at 5 wt% New Crystalline Ingrowth Level (Turcotte et al. 1980) and Detectable Crystallinity TTT Curve for Glass UK-189 (Malow et al. 1980)

The TTT curves actually represent rather complex processes, since two or three major phases are crystallizing with different time-temperature kinetics--each with its own "liquidous" temperatures. Semiquantitative data for specific phases are reported in most of the PNL references. The information on $(Ce,Re^{3+})O_{2-x}$ is particularly interesting, especially for glass 78-157, where it was the only observed crystalline product. The TTT curve generated for this glass, at four different (low) concentrations is given in Figure 7.5. Note that the crystallization at 950°C occurs in minutes, requiring rapid cooling through this temperature region to avoid precipitation. Figure 7.6 shows similar curves for glass 76-68 (and some data for UK-189), where crystallization of CeO_2 occurs at lower temperatures and requires anneals of 1 to 10 days.

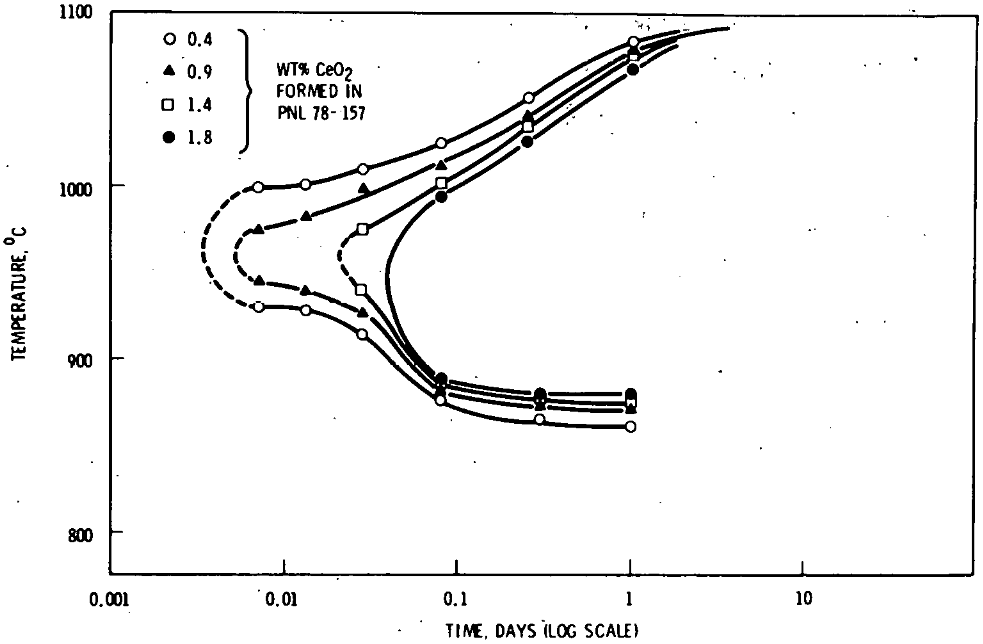


FIGURE 7.5. TTT Curves for Increasing Levels of CeO_2 Ingrowth in Glass PNL 78-157

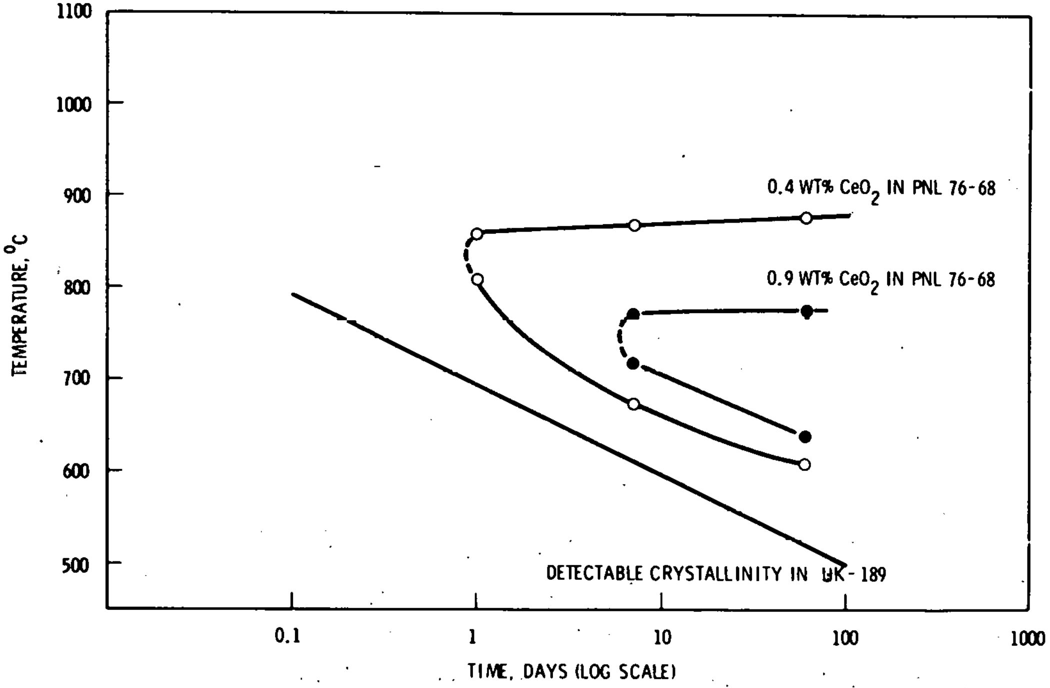


FIGURE 7.6. TTT Curves for Two Levels of CeO_2 Ingrowth in Glass PNL 76-68. Detectable crystallinity curve for glass UK-189 (from Malow 1980) shown for comparison with Figure 7.4.

Some qualitative data shown in Figure 7.7 have been reported by Araki (1981) that suggest behavior similar to that presented in Figures 7.4-6. The borosilicate glass composition (G-2, given in Table 7.1) was melted at 1200°C.

The information presently available for borosilicate waste glasses may be summarized/extrapolated in several ways. These glasses typically have dilatometric softening points usually between 500 and 600°C and melting temperature (200 poise) between 950 and 1150°C. Rate data plotted as 1/T and TTT plots appear to be useful in fitting experimental data obtained above the glass softening point. Although some of the needed information is for T <300°C and times >100 years, neither of these can be directly evaluated, since crystallization has not been observed at temperatures below 500°C, even in experiments ments lasting several years. The extrapolations proposed in Figure 7.8 are based on studies referenced in the present document and suggest the following generalizations.

- Crystal nucleation at 200°C (four curves) may be as short as 30 years for a low-melting glass like the phosphate glass D-P 78/7 or as long as 1000 years for the parent glass of the celsian glass ceramic D-B 1-3, which has a higher melting temperature.
- Significant crystallization (>5 wt%) could occur (200°C) as rapidly as 500 years for a glass like PNL 77-260 or "never" as for glass PNL 76-68.
- The time span between nucleation and significant crystal growth may be large, as the 0.4 and 5 wt% curves for glass PNL 76-68 imply. The extrapolations at 200°C imply 500 years for nucleation and millenia for growth.

7.1.4 Effects of Heat Treatment on Properties

In the final analysis, it is possible that crystallization of waste glass may have no detrimental effect on properties. Indeed, intentionally crystallized glass ceramics have been investigated by Lutze and coworkers at the Hahn-Meitner Institut, Berlin, as possible improvements over their parent glasses. As to chemical durability, it is clear from their studies (Dé et al. 1976a,b) that carefully crystallized glasses can be as durable as the parent glass.

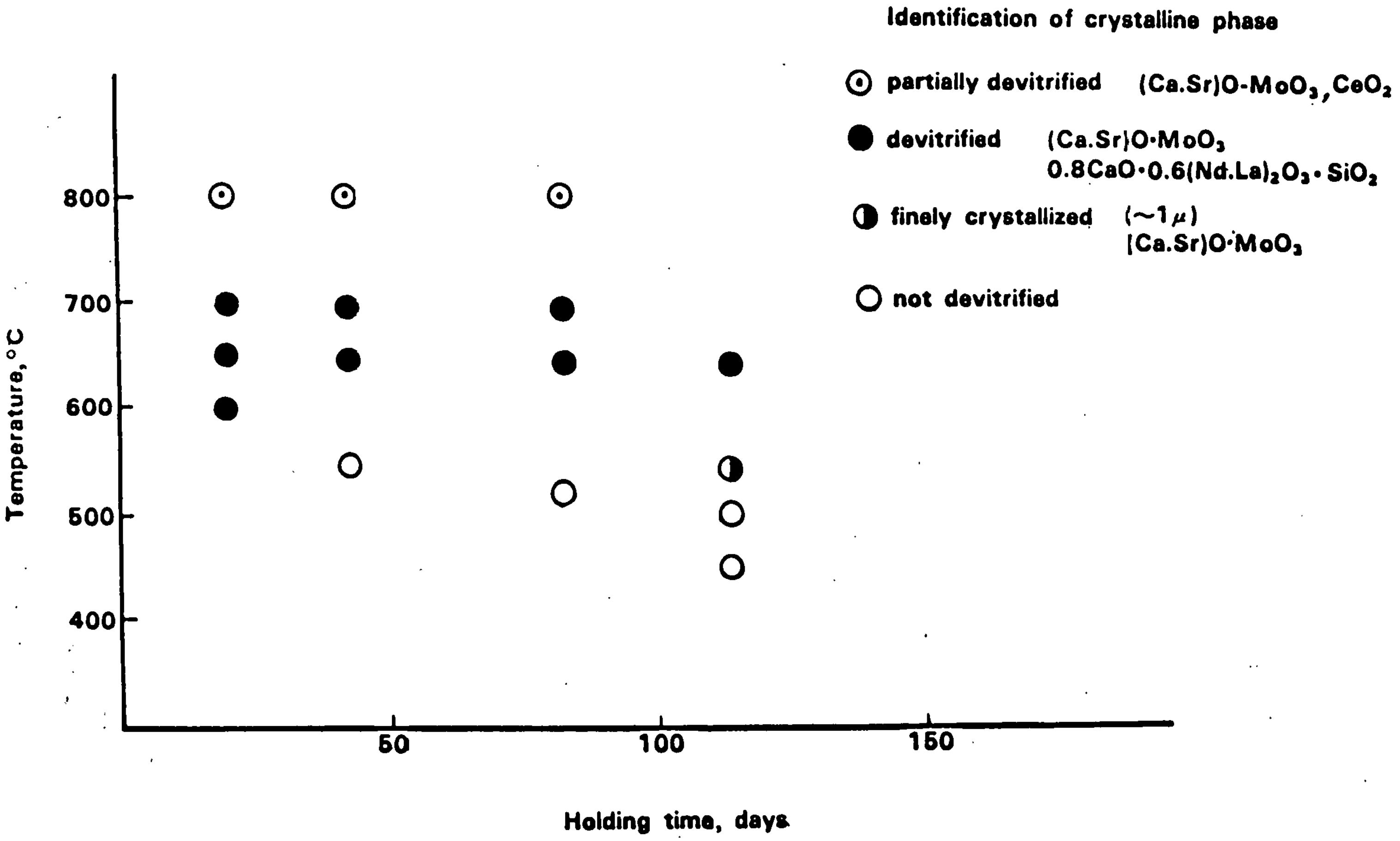


FIGURE 7.7. Effect of Heat Treatment Temperature and Holding Time on Devitrification of Glass G-2 (from Araki 1981)

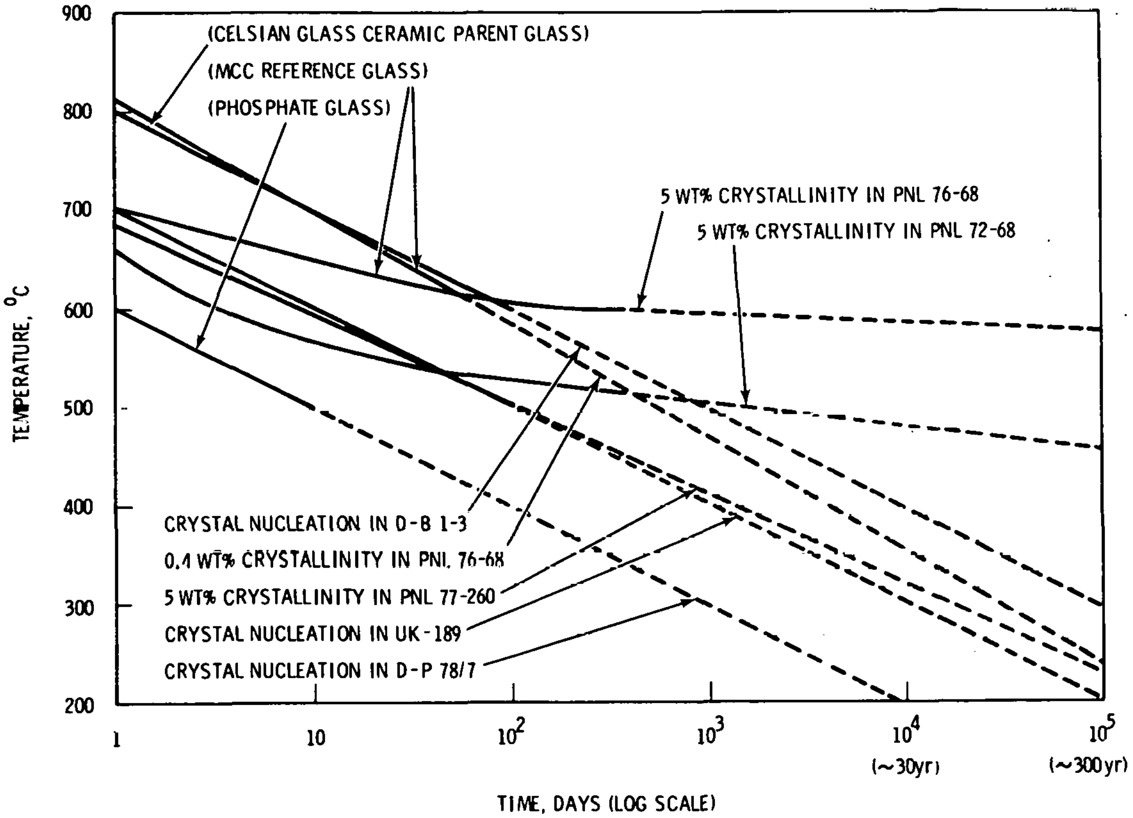
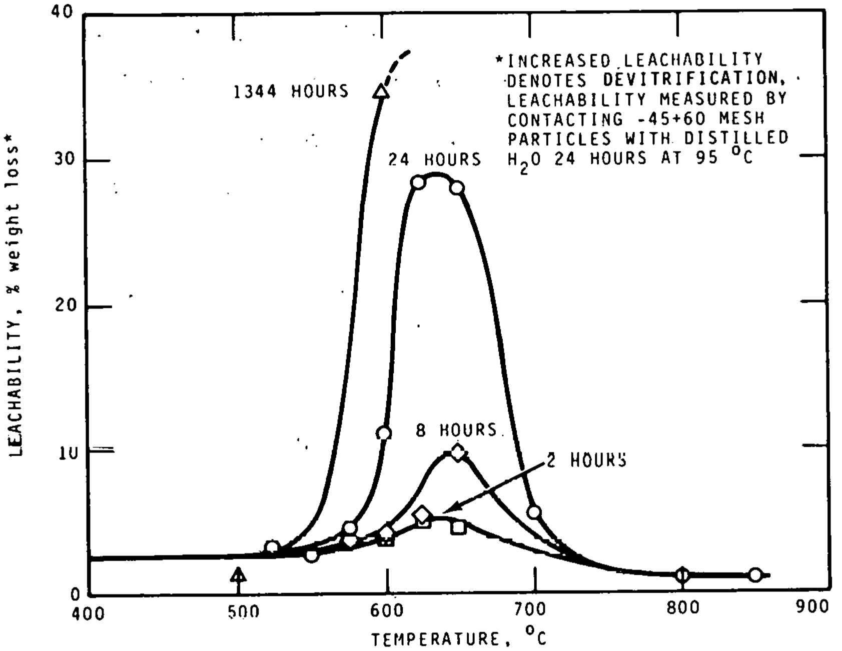


FIGURE 7.8. TTT Extrapolations of 1-day and 100-day Data to 10^5 Days for a Phosphate Glass, a Celsian Glass-Ceramic Parent Glass and Four Borosilicate Glasses

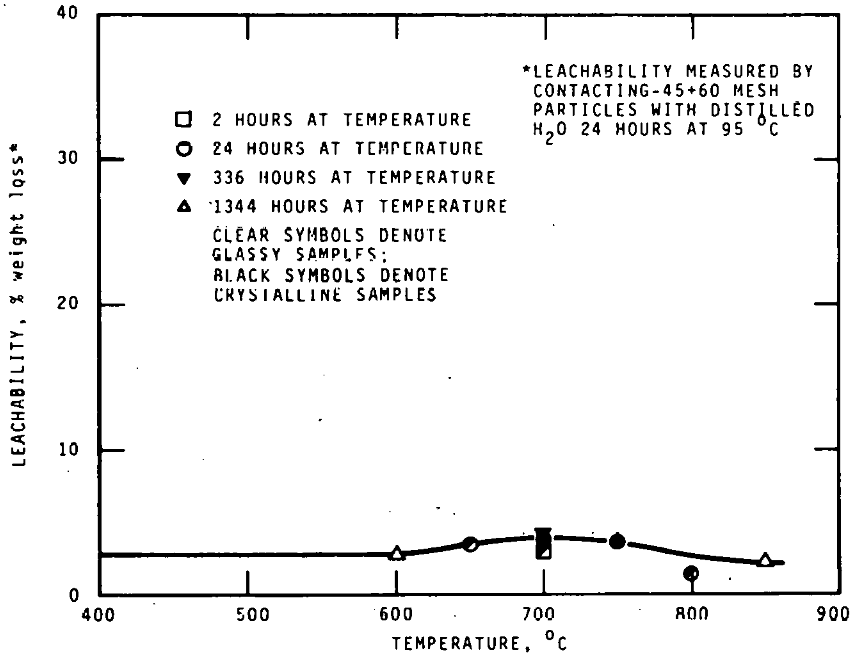
There are several possible effects of crystal growth in glasses, not specifically pointed out in the preceding sections. Usually, ingrowth of crystalline phases decreases residual glass phase concentrations of rare earth and transition elements, as well as zirconium and titanium; thus the residual glass is less chemically durable than the original glass. Much less often the new crystalline phases are also less durable (Lutze et al. 1979). Ingrowing crystals can also create strains large enough to cause microcracking, as reported for Zn_2SiO_4 ingrowth in glass 72-68 (Turcotte and Wald 1978). Concentration of some elements at crystal/glass boundaries may result in enhanced leachability. There are also secondary effects of generally unknown consequence related to localizing the radiation damage. For example, Weber et al. (1979) studied a partially devitrified glass in which the radiation-induced volume expansion of one phase ($Ca_3Gd_7(SiO_4)(PO_4)O_2$) led to microcracking of the parent glass. Other questions concerning the ability of crystalline phases to withstand transmutation (e.g., Cs → Ba) have not been answered.

With regard to experimental measurements of leach rate changes, phosphate glasses typically attain maximum devitrification growth in the temperature range of 500 to 700°C (Grover and Walmsley 1968). This devitrification causes an adverse change in leach rate that can span three orders of magnitude, as Figure 7.9 shows (Mendel and McElroy 1972). In this figure, the leach rates of a phosphate glass and a borosilicate glass are shown as functions of the same heat treatments. As suggested earlier, this comparison shifted research emphasis away from the phosphate glasses. Crystal yield data taken from the work by Turcotte and Wald (1978) are shown in Figure 7.10 for the growth of Zn_2SiO_4 and $SrMoO_4$ in glass PNL 72-68 over the temperature range of 400 to 1000°C for an annealing time of 2 months. The corresponding leach rates for this devitrified glass are shown in the upper curve of Figure 7.11 (Ross et al. 1978). It is readily apparent that the change in leach rate is directly related to devitrification. The elemental leach rates for vitreous and devitrified glass PNL 72-68 given in Table 7.4 indicate that the increase in leach rate observed after 2 months at 700°C is due to the formation of the $SrMoO_4$ phase in this glass. Additional leaching data reported by Mendel et al. (1977) support the conclusion that the increased leaching of devitrified glass is related to increased dissolution of $SrMoO_4$. An additional factor is that ingrowth of the Zn_2SiO_4 phase caused microcracking, thereby increasing the surface area and the apparent leach rate. Although most studies have been limited to evaluation of simulated HLW glass, Wald and Westsik (1979) produced radioactive samples of PNL glasses 72-68, 76-68, 77-107, and 77-260 and compared them to their respective simulated compositions in both the vitreous and devitrified states, as summarized in Table 7.5. Neither simulation nor devitrification appears to change the leach rate of the glasses by more than a factor of three from the values obtained for the radioactive vitreous samples.

Glass PNL 76-68 is the MCC reference borosilicate glass composition. Like PNL 72-68, it may be partially crystallized between 600 and 900°C (Ross et al. 1978), but to a lesser extent. Figure 7.12 shows a slight increase in



(a) Leach Rate of Phosphate Glass Increases as Heat Treatment Causes Devitrification



(b) There Is Little Change in Leach Rate as Heat Treatment Devitrifies This Borosilicate Glass

FIGURE 7.9. Glass Leach Rate as a Function of Heat Treatment Temperature and Holding Time for a) Phosphate Glass PW-2 and b) Borosilicate Glass IPM PW-4m (from Mendel and McElroy 1972)

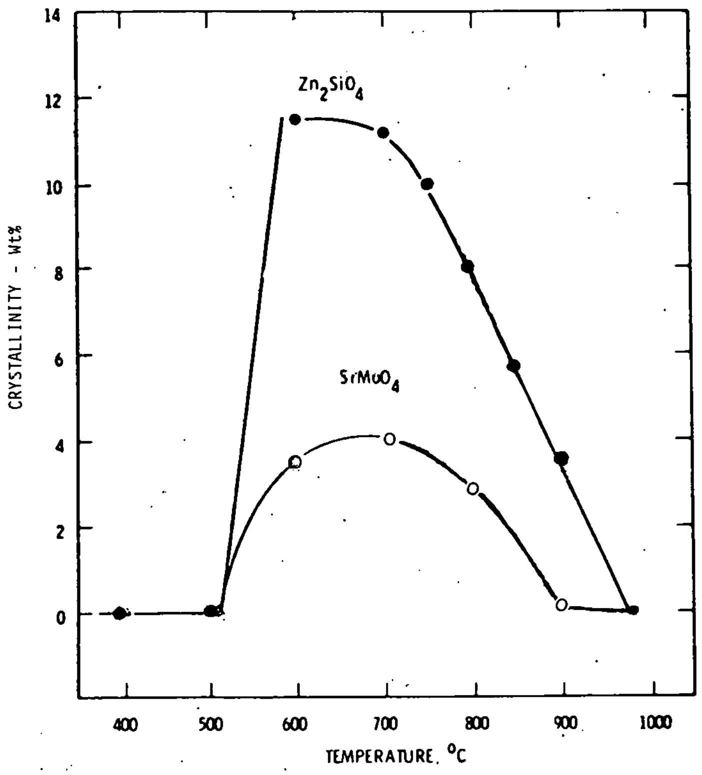


FIGURE 7.10. Ingrowth of Zn_2SiO_4 and $SrMoO_4$ as a Function of Temperature for Glass PNL 72-68 Heat-Treated 2 Months (Turcotte and Wald 1978)

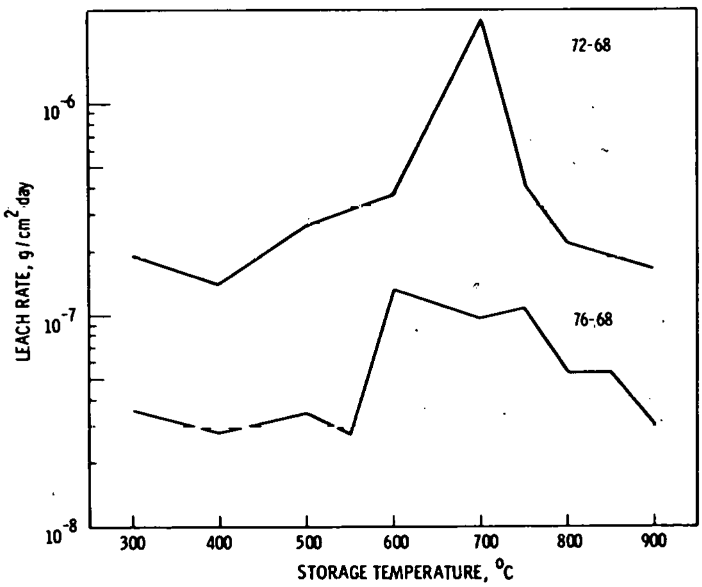


FIGURE 7.11. Long-Term Cesium Leach Rates of Glasses PNL 72-68 and 76-68 as a Function of Temperature for a 2-Month Heat Treatment (from Ross et al. 1978)

TABLE 7.4. Average Long-Term Leach Rates of Glass PNL 72-68 Before Heat Treatment (Vitreous) and After 2 Months at 700°C, g/cm^2-day (Ross et al. 1978)

Element Analyzed	Vitreous 1000°C 2 hr	Devitrified 700°C 2 mo
Ba	2.18×10^{-6}	1.53×10^{-6}
Cs	1.82×10^{-7}	2.43×10^{-6}
Mo	1.01×10^{-6}	1.28×10^{-6}
Sr	1.52×10^{-7}	1.12×10^{-6}
U	1.60×10^{-8}	6.86×10^{-8}
Zn	1.29×10^{-6}	8.17×10^{-9}
Zr	2.00×10^{-6}	4.95×10^{-7}

TABLE 7.5. Leach Rates of Four Full-Level and Four Simulated Nuclear Waste Glasses Based on Cs, Sr, and Eu$^{(a)}$ for Both Vitreous and Devitrified Samples (Wald and Westsik 1979)

	Cesium		Strontium,	Europium,
	Simulated	Radioactive	Simulated	Radioactive
PNL 72-68				
As prepared	9.0×10^{-6}	2.3×10^{-5}	6.9×10^{-6}	3.1×10^{-6}
Devitrified	3.2×10^{-5}	4.3×10^{-5}	1.5×10^{-5}	4.2×10^{-6}
PNL 76-68				
As prepared	2.7×10^{-6}	3.0×10^{-6}	2.8×10^{-6}	1.3×10^{-6}
Devitrified	3.0×10^{-6}	2.6×10^{-6}	3.3×10^{-6}	1.3×10^{-6}
PNL 77-107				
As prepared	6.4×10^{-6}	6.5×10^{-6}	6.5×10^{-6}	2.2×10^{-6}
Devitrified	8.0×10^{-6}	4.4×10^{-6}	6.0×10^{-6}	7.7×10^{-7}
PNL 77-260				
As prepared	9.1×10^{-7}	1.8×10^{-6}	1.4×10^{-6}	8.1×10^{-7}
Devitrified	9.8×10^{-7}	1.8×10^{-6}	1.2×10^{-6}	5.7×10^{-7}

(a) The leach rates in g/cm^2-day are average rates covering 8 through 84 days of testing (IAEA, 25°C).

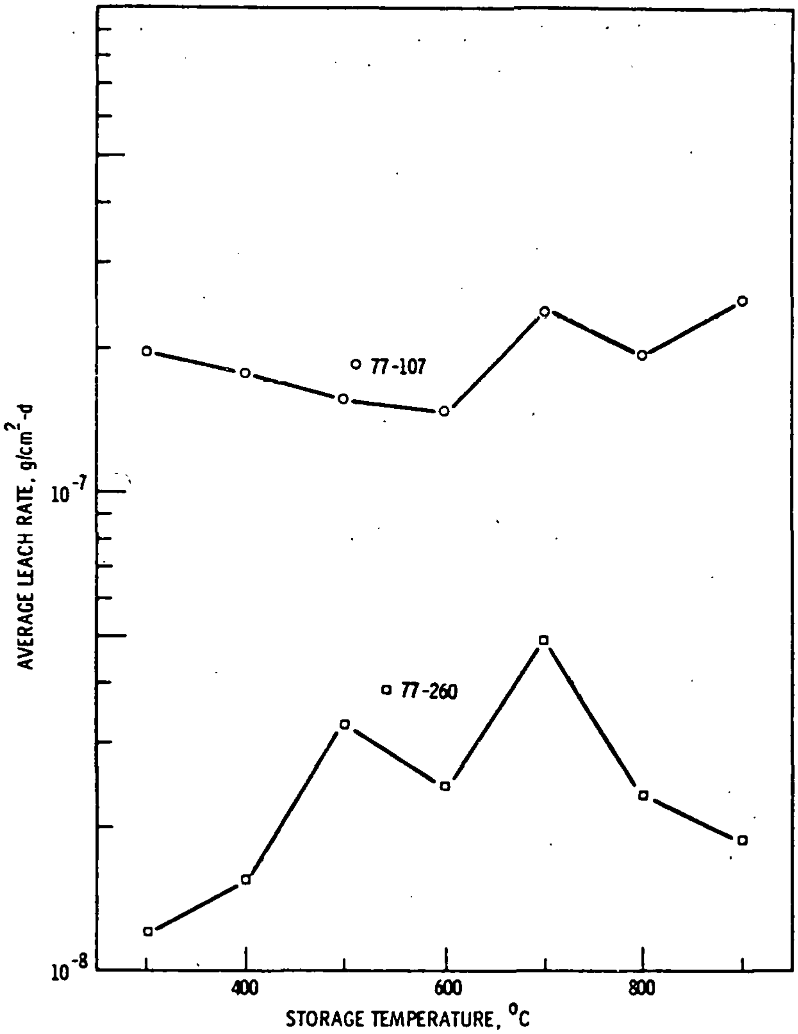


FIGURE 7.12. Long-Term Cesium Leach Rates of Glasses PNL 77-107 and 77-260 as a Function of Temperature for a 2-Month Heat Treatment (from Ross and Mendel 1979)

leach rate that corresponds directly to the extent of devitrification. The maximum leach rate change is by about a factor of five during long-term leach tests. The changes are also by about a factor of 5 based on Soxhlet leach data, as shown in Table 7.6 for glasses PNL 76-68, 77-107, and 77-260. Long-term leach data graphically shown in Figure 7.12 for glasses PNL 77-107 and 77-260 show much less variation for leach rate versus heat treatment. The microstructures of these three glasses (Table 7.6) differ from those of PNL 72-68 in that all show a dispersion of fine crystals with no evidence of

TABLE 7.6. Standard Soxhlet Leach Data[a] After Heat Treatment for Three Borosilicate Glasses (Ross et al. 1978)

Storage Temperature, °C	PNL 76-68					PNL 77-107				PNL 77-260			
	2 Hr	1 Day	1 Wk	2 Mo	1 Yr	2 Hr	1 Day	1 Wk	2 Mo	2 Hr	1 Day	1 Wk	2 Mo
1200	5.40					2.48				2.14			
1150						3.13				3.10			
1100	3.90					3.73				3.22			
1050	5.80					2.18				3.47			
1000	5.30					3.13				3.80			
900		5.02	8.41	7.50	7.45		2.72	1.86	1.85		4.19	2.53	4.40
850		3.92	4.0	4.60	8.00		2.00	3.51	2.29		2.68	6.60	5.00
800		4.90	5.72	5.80	9.40		2.53	2.34	1.90		3.30	5.50	7.30
750		7.09	7.70	8.60	8.00		2.56	2.53	2.05		2.89	4.71	5.70
700		4.05	5.00	6.50	5.61		2.45	2.00	3.31		5.13	6.88	3.00
650		7.47	3.73	11.70	3.70		2.28	2.81	2.03		3.46	3.03	2.70
600		7.97	8.70	5.80	4.90		3.60	1.66	2.16		3.26	2.31	3.20
550		4.20	6.80	6.60	5.66		1.60	3.15	3.50		2.10	5.33	2.40
500		4.54	6.20	11.20	7.20		2.97	2.50	1.63		2.60	4.25	1.90
400				6.50	1.80				2.56				4.10
300				6.80	4.90				2.31				3.60

(a) Leach rate in % weight loss in 72 hr. Convert to g/cm^2-day by multiplying by 1.28 x 10^{-5}.

microcracking or formation of a soluble phase. Densities of the partially crystallized samples did not change significantly from the parent glass (Westsik 1979). Malow et al. (1980) reported the effects of devitrification on leach rate for six glass compositions. In all cases, as shown in Figure 7.13, there is an increase in leach rate with devitrification. For UK-209 the increase is small; for SON 58.30.20.U2 the increase is nearly one order of magnitude.

It seems clear that leach rates of borosilicate glass compositions in the worst cases increase by about a factor of 10, as a result of devitrification. In most cases the changes are less than a factor of five, and in some cases are negligible.

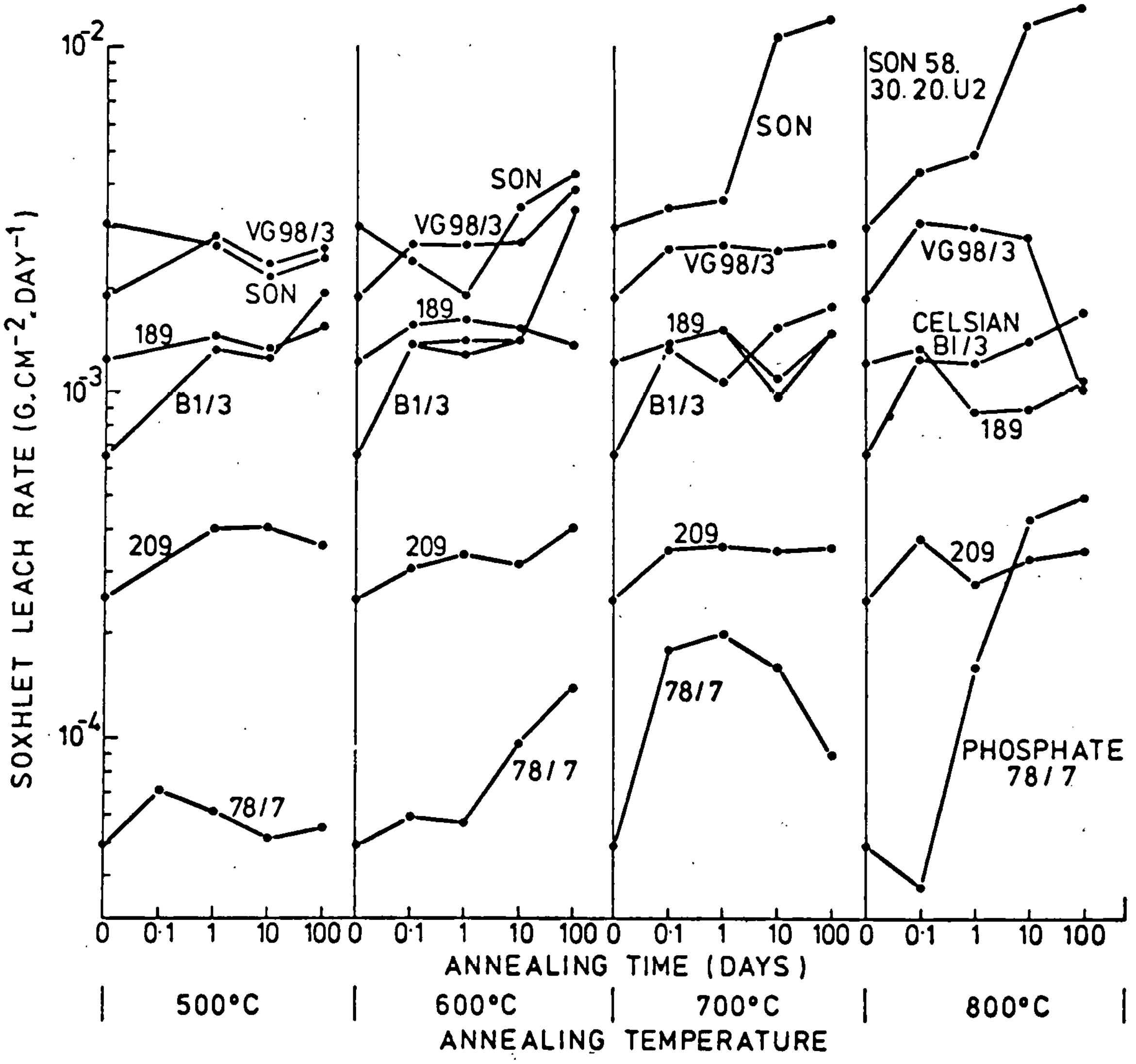


FIGURE 7.13. Soxhlet Leach Rates of Four European Borosilicate Glasses (SON 58.30.20 U2, VG 98/3, UK 189 and UK 209), One Phosphate Glass (P 78/7), and the Celsian Glass Ceramic B1-3, as Functions of Heat-Treatment Temperature and Holding Time (from Malow et al. 1980)

7.2 CRYSTALLINE WASTE FORMS

Various crystalline waste forms have been considered for immobilization of nuclear wastes, extending to both extremes of the possible thermal treatment scale. High-temperature, fully crystallized composites such as "SYNROC," glass-ceramics, and cast/hydrated ceramics such as "FUETAP" have all been suggested as promising HLW forms for one reason or another. Since many of these forms have been under development for only a few years, very little information is available in several areas, compared to that for waste glasses.

As to thermal stability, high temperature-fired ceramics very likely will not undergo significant change when subjected to lower temperature treatment, even for extended times. It could be postulated that polymorphic phase changes might occur for certain phases in crystallized forms. For glass ceramics, however, some microstructural coarsening and ingrowth of minor phases (in the residual glass matrix) could be expected and have been observed (Malow et al. 1980). The cementitious waste forms may lose water of hydration at relatively low temperatures and undergo measurable physical and chemical changes. The magnitude and importance of these changes in hydrated forms has not, however, been reported. There is understandably less information on thermal stability of the other crystalline ceramics, since their preparation may well have required annealing at 1200°C and further low-temperature studies seem unnecessary.

Table 7.7 lists the primary crystalline waste form candidates for which some phase analyses have been reported, along with a listing of primary phases present and their concentrations (%) when available. The table is intended to be representative rather than inclusive. Only one example of SYNROC is presented, for example, although many different compositions have been reported. More information, including other compositions, appears in the following sections. A concise summary of the processes involved in manufacturing most of these forms (for TRU wastes) along with summaries of major properties has been recently reported (Crisler 1980).

7.2.1 Observed Phases and Changes with Heat Treatment

7.2.1.1 Glass Ceramics

Dé et al. (1976a,b), Lutze et al. (1979) and Malow et al. (1980) have reported on the development and properties of several glass-ceramic compositions. They reported that thermal annealing of the celsian B1-3 compositions led to formation of $BaMoO_4$ and coarsening of the microstructure as the major phase ($BaAl_2SiO_2O_8$) transforms from a hexagonal to monoclinic structure and that

TABLE 7.7. Major Phases of Some Crystalline Waste Forms

Crystalline Waste Form	Major Phases (by mineral name)
Supercalcine (SPC-4)	Apatite, monazite, fluorite, pollucite, scheelite, corundum, spinel, rutile
SYNROC (B)	Hollandite(35), perovskite(22), zirconolite(31)
Celsian glass-ceramic (B1-3)	Cymrit (or h- or m-celsian) pollucite RE-titanate, Ba-molybdate
Cermet	Ni-Fe alloy, [unspecified ceramics]
FUETAP and concrete	Portlandite, alite

these crystals then grow larger. The compositions and observed phases for the celsian and fresnoite glass ceramics are given in Table 7.8. The fresnoite glass ceramic was thermally stable over the same temperature range that the celsian glass ceramic was studied.

Oguino et al. (1979) studied the production of the six different glass ceramics whose compositions and observed phases are given in Table 7.9. Changes in the glass ceramics when further heat-treated at 700°C are given in Table 7.10. Four of the six glasses showed no effects from heat treatment, while in one additional Li_2SiO_3 formed and in the P-50 glass ceramic a $NaAlSiO_4$ phase precipitated.

7.2.1.2. High-Temperature Ceramics

Sandia Titanate Ceramics. Johnstone et al. (1979) characterized their titanate product as shown in Table 7.11. Heat treatment of this material at 1200°C for 19 hr led to the formation of several unidentified phases and the disappearance of two previously observed but unidentified phases. These phase transformations may have occurred as the composition changed in response to volatility losses. Another sample was heat-treated at 800°C for 475 hr. This sample developed two alteration zones on its periphery, principally due to the volatility of ruthenium and cesium and secondarily to the migration of sodium to these alteration zones. The interior of the specimen showed some coarsening of the microstructure but no other changes.

TABLE 7.8. Composition and Properties of Celsian and Fresnoite Glass Ceramics (from W. Lutze et al. 1979)

	Celsian Types, wt%	Fresnoite Types, wt%
SiO_2	28 - 38	22 - 28
Al_2O_3	10 - 13	0 - 2
B_2O_3	2 - 7	0 - 3
CaO	0 - 6	0 - 4
BaO	13 - 16	28 - 36
Na_2O	0 - 2	-
Li_2O	1 - 3	-
TiO_2	3 - 4	14 - 23
ZnO	3 - 5	0 - 6
PbO	0 - 3	-
Waste oxides	20	20
Melting temp., K	1450 ± 50	1475 ± 25
100 poise temp., K	1350 - 1450	1400 - 1500
Electr. cond. $(\Omega\ cm)^{-1}$ at prep. temp.		
Nucleation temp., K	900 ± 25	975 + 25
Nucleation time, hr	3	3
Cryst. temp., K	1075 - 1125	1125 - 1125
Cryst. time, hr	10 - 15	10 - 15
Heat conductivity, $W\ m^{-1}\ K^{-1}$ (500-900 K)	1.2 - 1.4	1.2 - 1.4
Transform. temp., K T_g, K	775 - 875	925 - 950
Dilatom. soft. point, K	$\geq$1000	$\geq$1000
Coeff. of thermal exp. $x10^7$	80 - 100	80 - 100
Crystal phases	Cymrit or h-Celsian m-Celsian (Ba) $BaAl_2Si_2O_8$ RE-Titanate (RE,An,Sr) $Re_2Ti_2O_7$ Ba-Molybdate (Mo,Ba) $BaMoO_4$ Pollucite (Cs,Rb) $(Cs,Na)AlSi_2O_6$	Fresnoite (Ba,Sr) $Ba_2TiSi_2O_8$ Priderite (Ba) $K_2Fe_2Ti_6O_{16}$ RE-Titanate (RE,An,Sr) $RE_2Ti_2O_7$ Ba-Molybdate (Ba,Mo) $BaMoO_4$

TABLE 7.9. Compositions and Crystal Phases of Glass-Ceramic (from Oguino et al. 1979)

	Sample No.					
	D-62, wt%	C-27, wt%	P-50 wt%	E-63, wt%	D-210, wt%	P-71, wt%
SiO_2	47.5	35.0	30.0	50.0	41.02	40.0
Al_2O_3	6.8	15.0	10.0	12.5	8.20	6.5
B_2O_3		5.0	5.0		3.50	3.5
Fe_2O_3	9.5				8.70	
TiO_2	2.7	5.0	10.0	6.0	3.20	10.0
CaO	6.8	4.0	25.0		4.10	10.0
MgO	6.8				1.37	
BaO		13.3				
ZnO		2.7		4.0		
Li_2O				7.5		
HLW	20.0	20.0	20.0	20.0	30.0	30.0
Total	100.0	100.0	100.0	100.0	100.0	100.0
Crystal phases	Fe_3O_4(a) $CaMoO_4$(a) $CaTiO_3$(a)	$CaMoO_4$(b) $CaTiO_3$(b)	$CaSiO_3$(c) $CaMoO_4$(c) Sphene(c)	Li_2SiO_3(d)	$CaMoO_4$(a) Fe_3O_4(a) $CaTiO_3$(a)	$CaMoO_4$(e)
Heat treatment	1100°C 1 hr	850°C 1 hr	900°C 3 hr	800°C 2 hr	900°C 1 hr	900°C 1 hr

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(a) Diopside ($CaO \cdot MgO \cdot 2SiO_2$)
(b) hexa-Celsian ($BaO \cdot Al_2O_3 \cdot 2SiO_2$)
(c) Perovskite ($CaTiO_3$)
(d) β-Spodumene ($Li_2O \cdot Al_2O_3 \cdot 4SiO_2$)
(e) Sphene ($CaO \cdot TiO_2 \cdot SiO_2$

TABLE 7.10. Changes of Crystal Phases and Leach Rate of Glass-Ceramics After Heating at 700°C for 1000 and 3000 hr (from Oguino et al. 1979)

Sample No.	Description of X-Ray Trace	Leach Rate, Weight Loss, $g/cm^2/day$		
		0 hr	1000 hr	3000 hr
D-62	No change	3.6×10^{-5}	3.6×10^{-5}	3.6×10^{-5}
C-27	No change	1.8×10^{-4}	1.9×10^{-4}	
P-50	Precipitate of $NaAlSiO_4$, appearance of sphene (111) peak	5.6×10^{-4}	8.5×10^{-4}	1.6×10^{-3}
E-63	Increase of intensity in Li_2SiO_3 (110) peak	2.1×10^{-4}	5.6×10^{-4}	
D-210	No change	6.5×10^{-4}	6.5×10^{-5}	6.6×10^{-5}
P-71	No change	1.2×10^{-4}	9.3×10^{-5}	

TABLE 7.11. Primary Containment Phases Identified[a] in SLA Titanate-Ceramics

Phase	Energy-Dispersive Elemental Analysis	Est. Vol. Fraction, %
TiO_2 (rutile)	Ti	50
Amorphous silica (SiO_2)	Si (trace U, Ti, Al, Na)	5
$Cs_2O \cdot Al_2O_3 \cdot 4SiO_2$ (dehydrated pollucite)	Si, Al, Cs (trace Ti, Rb)	1
$Gd_2Ti_2O_7$ (some U, Nd) (trace Zr, Y)	Ti, Gd	10
Elemental Mo	Mo (trace Fe, Ti)	5
Elemental Pd	Pd (some Te and Ti) (trace Fe, Mo)	2
Cubic-ZrO_2	Zr (trace U, Si)	5
Amorphous zeolite (Na, Cs) alumino-silicate	Na, Cs, Al, Si (trace Ti, U, Fe, Mo, Gd, Sr)	10

(a) At least eight more distinct phases have been detected by electron diffraction and/or x-ray energy-dispersive analysis. These have not been identified, but most appear to be titanates.

Supercalcine. Table 7.12 lists the compositions and phases reported for supercalcines SPC-2 and SPC-4 by McCarthy et al. (1979). A recent report by Lokken (1980) includes heat-treatment studies, but directed more toward determining optimum processing conditions for sintering (i.e., initial crystal nucleation and growth) rather than assessing further phase changes occurring during additional heat treatments after processing. The thermal stability data reported by McCarthy (1976) were from 1200°C heat treatments, where the phase changes occur because of vaporization. This work did show that the pollucite phase is unstable in the presence of $SrRuO_3$ at 1200°C. As cesium and ruthenium are volatilized, then the $CsAlSi_2O_6$ and $SrRuO_3$ convert to $Sr_2Al_2SiO_7$ and $SrSiO_3$.

TABLE 7.12. Compositions and Major Phases of Supercalcine-Ceramics, wt% (adapted from McCarthy et al. 1979)

Oxide	SPC-2	SPC-2+U	SPC-4	SPC-4+U
Waste				
U_3O_8		16.5		16.8
CeO_2	16.3	13.7	6.8	5.6
RE_2O_3(a)	19.0	15.9	30.2	25.2
ZrO_2	7.6	6.4	7.8	6.5
MoO_3	8.0	6.7	8.2	6.8
P_2O_5	4.2	3.5	4.3	3.5
BaO	2.4	2.0	2.5	2.1
SrO	1.6	1.4	1.7	1.4
Cs_2O	4.5	3.7	4.6	3.8
Rb_2O	0.5	0.4	0.6	0.5
Na_2O	0.2	0.1	0.2	0.2
RuO_2	0.5	0.4	0.5	0.4
Fe_2O_3	4.7	3.9	4.8	4.0
Cr_2O_3	0.5	0.4	0.5	0.5
NiO	0.2	0.2	0.2	0.2
CdO	0.2	0.1	0.2	0.1
Ag_2O			0.1	0.1
Additives				
CaO	4.9	4.1	2.1	1.7
SrO	1.2	1.0	2.6	2.1
Al_2O_3	4.4	3.7	4.5	3.8
SiO_2	19.1	15.9	17.6	14.7
Waste loading	70.5%	75.3%	73.2%	77.7%

(a) RE = La, Pr, Nd, Sm, Eu, Gd, Y (plus RE as a stand-in for Am + Cm).

Supercalcine Crystalline Phases

Nominal Composition	Structure Type
$(Ca,Sr)_2RE_8(SiO_4)_6O_2$	Apatite
$REPO_4$	Monazite
$(U,Ce,Zr,RE)O_{2\pm x}$	Fluorite
$(Cs,Rb,Na)AlSi_2O_6$	Pollucite
$(Ca,Sr,Ba)MoO_4$	Scheelite
$(Fe,Cr)_2O_3$	Corundum
$(Ni,Fe)(Fe,Cr)_2O_4$	Spinel
RuO_2	Rutile

SYNROC. SYNROC is a high-temperature, highly crystalline ceramic waste form proposed by Ringwood and Kesson (1979). Table 7.13 gives the compositions for SYNROC A and B (Rusin 1980). SYNROC B, which is favored over A, is composed of only three titanate phases: hollandite (35%), zirconolite (31%), and perovskite (22%). However, composition development work on this proposed waste form is still proceeding as Reeve et al. (1981) report the development of SYNROC C and Newkirk et al. (1981) the development of SYNROC D. But except for hydrothermal tests, no thermal stability experiments have been reported for any SYNROC compositions.

TABLE 7.13. Composition of SYNROC A and SYNROC B

	SYNROC A	SYNROC B[(a)]
Radwaste, wt%	10	10
Inert additives, wt%	90	90
	Composition of Inert Additives, wt%	
SiO_2	13	--
TiO_2	33	60.4
ZrO_2	10	9.9
Al_2O_3	16	11.0
CaO	6	13.9
BaO	17	4.2
SrO	--	--
NiO	--	0.6
Na_2O	--	--
K_2O	5	--
Mineral structures	"Hollandite," perovskite, zirconolite, Ba-felspar, kalsilite, leucite	"Hollandite," perovskite, zirconolite

---

(a) "Hollandite" 35%, zirconolite 31%, perovskite 22%, plus additional TiO_2 (7%) and Al_2O_3 (5%) required for incorporation of radwaste components into SYNROC minerals.

Cermet. Aaron, Quinby and Kobisk (1980) have reported development studies on this crystalline waste-form. Pellets of unspecified ceramic phases are embedded in a nickel-iron alloy matrix. At this stage of development no thermal stability data have been reported.

7.2.1.3 Cementitious Forms

Concrete. A recent review of concrete as a medium for immobilization of radioactive waste has been written by Lokken (1978). Several other studies have been published since then (Witte and Koster 1979; Roy et al. 1979; Jantzen and Glasser 1979); however, no phase characterization is reported. Thermal stability studies of concrete have typically been limited to evaluation of water losses from the cured waste form much as in Stone (1979). The topic of "curing" the concrete as applied to waste fixation lacks quantitative data in terms of formation kinetics, and there are no data reported on thermal phase transformations that occur after curing.

Wald et al. (1980) have identified $Ca(OH)_7$ and Ca_3SiO_5 as major crystalline phases occurring in two Portland type II cements used for waste immobilization. The first cement was prepared with 10% PW-9 calcine and the second with 10% SPC-5B supercalcine.

FUETAP and Hot-Pressed Concrete. A special category of concretes has been investigated as reported by Moore et al. (1979). These are concretes formed under elevated temperature and pressure (FUETAP). A similar approach involving hot-pressed concrete has been reported by Roy and Gouda (1978). While the effects of a heat treatment on physical strength are reported for several hot-pressed concretes (see Section 7.2.2.3), there are no kinetic or phase-transformation data available.

7.2.2 Heat-Treatment Effects on Properties

7.2.2.1. Glass Ceramics

Increases in leach rate by a factor of two (Lutze et al. 1979) or five (Malow et al. 1980) result when extended heat treatment of the glass-ceramic causes microstructural coarsening. The ingrowth of new phases can cause a corresponding increase in leach rate if the new phase either is soluble or leaves the residual glass more susceptible to attack. The leach rate of glass-ceramic P-50 (Table 7.9, Oguino et al. 1979) increases as $NaAlSiO_4$ forms. This phase depletes the residual glass of aluminum, and the boron-enriched residual glass becomes less leach-resistant as this crystalline phase forms.

7.2.2.2 High-Temperature Ceramics

Changes in materials properties after heat-treatment have essentially not been studied except with respect to phase changes associated with volatility losses, as mentioned in the previous section. The importance of these changes with respect to other properties, such as leach rate, have not been studied.

7.2.2.3 Cementitious Forms

Portland type II cements with 10% PW-9 calcine increase in density as water is evolved, as Figure 7.14 shows. Lokken (1978) reports that heat-treatment at >300°C results in a gradual loss of compressive strength (up to 80% loss) after an initial increase. A loss of about 25% of the compressive strength of concrete was also reported when it was heat-treated at 100°C for 3 months (Lokken 1978).

Hot-pressed concretes were reported by Roy and Gouda (1978) to retain their original strength even after prolonged heat treatment (28 days at 230°C). No other effects on properties attributable to heat treatment of concrete have been reported.

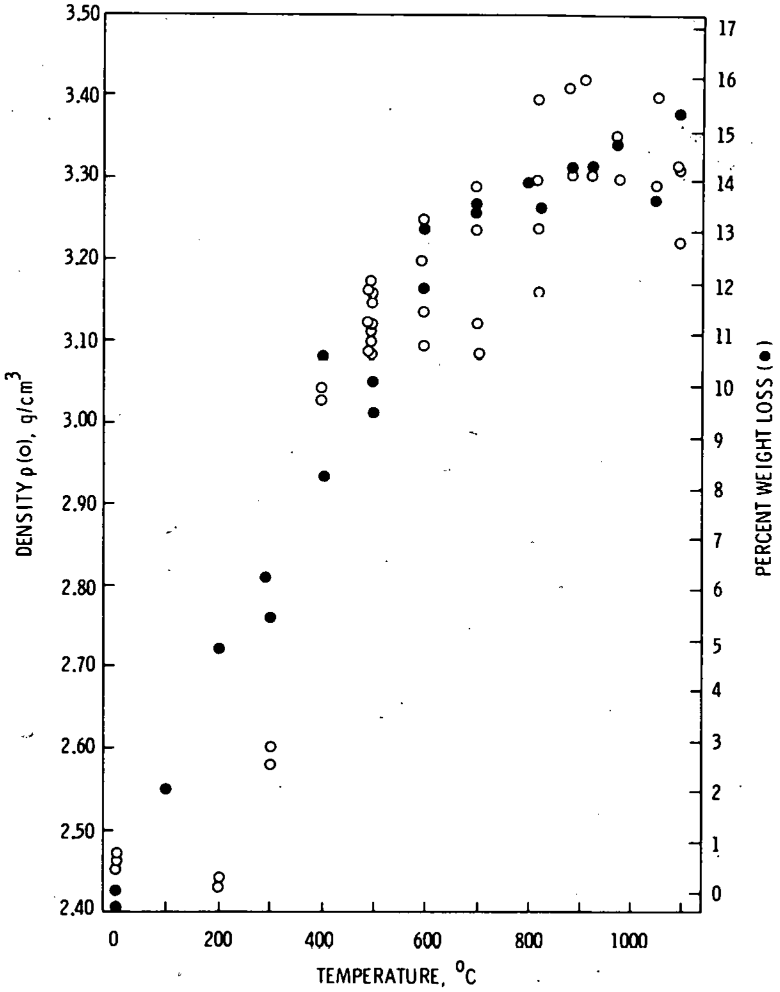

FIGURE 7.14. Bulk Density Changes and Sample % Weight Loss as a Function of Temperature for Portland Type II Cement (with 10% PW-9 calcine) Annealed 4 Days

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